VOLUME 35 JUNE 1957 NUMBER 6

Canadian Journal of Chemistry

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OTTAWA CANADA

CANADIAN JOURNAL OF CHEMISTRY

(Formerly Section B, Canadian Journal of Research)

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Canadian Journal of Chemistry

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOLUME 35 JUNE 1957 NUMBER 6

SOME ARALKYL AND ARYL ALKYL SULPHIDES AND DISULPHIDES[1]

MARSHALL KULKA AND F. G. VAN STRYK

ABSTRACT

Sixty sulphides and disulphides have been prepared from mercaptans and alkyl and alkylene halides for testing as insecticides.

In a co-operative program of insecticide research, a series of sulphides and disulphides were synthesized in this laboratory and screened for aphicide action at the Ontario Agricultural College by Professor A. J. Musgrave and Mr. I. Kukovica (10). This paper describes the preparation and some reactions of these compounds.

The method of Patterson and du Vigneaud (12), which comprises heating the mercaptan (I) in the presence of alkali with a large excess of ethylene dichloride, was employed in the preparation of the aralkyl 2-chloroethyl sulphides (II) listed in Table I:

$$\underset{\text{I}}{RSH} + NaOCH_3 + ClCH_2CH_2Cl \rightarrow \underset{\text{II}}{RSCH_2CH_2Cl} + NaCl + CH_3OH$$

Aralkyl 3-bromopropyl sulphides could not be obtained by this method from 1,3-dibromopropane because at some stage during the reaction with the benzyl mercaptan (I) dehydrohalogenation occurred and the aralkyl allyl sulphide formed. When two moles of the mercaptan (7) and one mole of the alkylene dichloride were allowed to react the product was the disulphide (III) (Table V):

$$2RSH + 2NaOCH_3 + Cl(CH_2)_nCl \rightarrow \underset{\text{III}}{RS(CH_2)_nSR} + 2NaCl + 2CH_3OH$$

It is known that sodium alkoxides react with trichloroethylene to give α,β-dichlorovinyl ethers (6). Also Cusa and McCombie (4) have provided evidence that the reaction product of thiophenol and trichloroethylene has the α,β-dichlorovinyl sulphide structure (IV).

$$\underset{\text{I}}{RSH} + NaOCH_3 + Cl_2C{=}CHCl \rightarrow \underset{\text{IV}}{RSCCl{=}CHCl} + NaCl + CH_3OH$$

On this basis it was concluded that the reaction products of benzyl mercaptans (I) and trichloroethylene recorded in Table IV are α,β-dichlorovinyl benzyl sulphides (IV) and not the β,β-dichlorovinyl sulphides.

2-(*p*-Chlorophenylmercapto) cyclohexanone (V), which was readily obtained from *p*-chlorothiophenol and 2-chlorocyclohexanone, proved to be a good source for ω-*p*-chlorobenzenesulphonylhexanoic acid (VII). The sulphone VI, obtained by hydrogen

[1]*Manuscript received February 13, 1957.*
Contribution from the Dominion Rubber Company Limited Research Laboratories, Guelph, Ont.

TABLE I

THE PREPARATION OF 2-CHLOROETHYL SULPHIDES, $RSCH_2CH_2Cl$ (II), FROM THE CORRESPONDING MERCAPTANS, RSH (I), AND ETHYLENE DICHLORIDE

$RSCH_2CH_2Cl$ R =	M.p. or b.p.	n_D^{20}	Yield, %	Empirical formula	Analyses			
					Calc.		Found	
					C	H	C	H
p-Chlorobenzyl	b_{12} = 163–164	1.5822	80	$C_9H_{10}Cl_2S$	48.87	4.52	49.19	4.49
2,4-Dichlorobenzyl	b_{12} = 182–185	1.5940	85	$C_9H_9Cl_3S$	42.27	3.52	42.50	3.61
3,4-Dichlorobenzyl	b_{12} = 186–189	1.5953	88	$C_9H_9Cl_3S$	42.27	3.52	42.05	3.51
2,4-Dimethylbenzyl	b_{13} = 155–157	1.5573	74	$C_{11}H_{15}ClS$	61.55	7.00	61.27	7.21
4,4′-Dichlorobenzhydryl	$b_{0.1}$ = 165	1.6088	85	$C_{15}H_{13}Cl_3S$	54.32	3.92	54.06	3.99
α-Naphthylmethyl	Not purified							
3-Phenylpropyl	b_{12} = 160–162	1.5500	65	$C_{11}H_{15}ClS$	61.55	6.99	62.59	7.13
3-*p*-Chlorophenylpropyl	b_{13} = 195–200	1.5644	85	$C_{11}H_{14}Cl_2S$	53.01	5.62	53.20	5.55
4-*p*-Chlorophenoxybutyl	b_1 = 165	1.5570	90	$C_{12}H_{16}OCl_2S$	51.61	5.73	51.91	5.59
p-$(ClCH_2CH_2SCH_2)_2C_6H_4$*	m.p. 73–74		40	$C_{12}H_{16}Cl_2S_2$	48.83	5.43	49.11	5.42

**Prepared from p-xylylene dimercaptan and ethylene dichloride.*

TABLE II

THE PREPARATION OF $RSCH_2CH_2SCN$ BY HEATING $RSCH_2CH_2Cl$ (II) WITH ALCOHOLIC KSCN FOR A FEW HOURS

$RSCH_2CH_2SCN$ R =	B.p. or m.p.	n_D^{20}	Yield, %	Empirical formula	Analyses: Calc. C	Calc. H	Found C	Found H
p-Chlorobenzyl	b_1 = 155–158	1.6065	90	$C_{10}H_{10}NClS_2$	49.28	4.11	49.30	4.16
2,4′-Dichlorobenzyl	$b_{0.2}$ = 158–160	1.6200	82	$C_{10}H_9NCl_2S_2$	43.17	3.24	43.29	3.28
3,4-Dichlorobenzyl	$b_{0.2}$ = 165–167	1.6240	85	$C_{10}H_9NCl_2S_2$	43.17	3.24	42.92	3.25
α-Naphthylmethyl	m.p. 62–63			$C_{14}H_{13}NS_2$	64.87	5.02	64.74	4.80
3-Phenylpropyl	$b_{0.5}$ = 138–140	1.5892	70	$C_{12}H_{15}NS_2$	60.76	6.33	60.58	6.56
3-*p*-Chlorophenylpropyl	$b_{0.5}$ = 160–164	1.5960	90	$C_{12}H_{14}NClS_2$	53.04	5.16	53.55	5.30
p-$(NCSCH_2CH_2SCH_2)_2C_6H_4$	m.p. 70–71		86	$C_{14}H_{16}N_2S_4$	49.41	4.70	49.79	4.68
2,5-Dichlorophenyl (I)	b_{12} = 216–219	1.6229	62	$C_9H_7NCl_2S_2$	40.91	2.65	40.50	2.64

TABLE III

PREPARATION OF $RYCH_2CH_2SCH_2CH_2YR$ (XI) FROM BIS-2-CHLOROETHYL SULPHIDE AND PHENOLS OR THIOPHENOLS (RYH)

$RYCH_2CH_2SCH_2CH_2YR$ RY =	M.p.	Yield, %	Empirical formula	Analyses: Calc. C	Calc. H	Found C	Found H
p-Chlorophenoxy	56–57	52	$C_{16}H_{16}O_2Cl_2S$	55.98	4.67	56.52	4.90
p-Chlorophenylmercapto	81–82		$C_{16}H_{16}Cl_2S_3$	51.20	4.27	51.22	4.27
p-*t*-Butylphenoxy	41–42	45	$C_{24}H_{36}O_2S_2$	74.61	8.81	74.90	8.51
4-Chloro-2-acetylphenoxy	114–115	60	$C_{20}H_{20}O_4Cl_2S$	56.20	4.68	56.69	4.94
2-Methoxy-4-formylphenoxy	131–132	48	$C_{20}H_{22}O_6S$	61.53	5.64	61.88	5.83
2-Mercaptobenzothiazolyl	71–72	50	$C_{18}H_{16}N_2S_5$	51.44	3.81	51.30	3.84

TABLE IV

PREPARATION OF SULPHIDES FROM MERCAPTANS AND ALKYL HALIDES

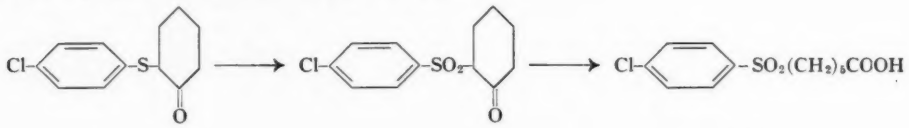
Sulphide prepared	Reactants	M.p. or b.p.	n_D^{20}	Yield, %	Empirical formula	Analyses			
						Calc.		Found	
						C	H	C	H
p-$ClC_6H_4CH_2SCH_2CH{=}CH_2$	*p*-$ClC_6H_4CH_2SH$ $ClCH_2CH{=}CH_2$	b_{13} = 140	1.5732	88	$C_{10}H_{11}ClS$	60.45	5.54	60.14	5.50
p-$ClC_6H_4CH_2SCH_2CH{=}CCH_3$ (Cl)	*p*-$ClC_6H_4CH_2SH$ $ClCH_2CH{=}CClCH_3$	b_{12} = 176–177	1.5800	92	$C_{11}H_{12}Cl_2S$	53.44	4.86	53.37	4.58
p-$ClC_6H_4CH_2SCH_2CHCH_2Cl$ (OH)	*p*-$ClC_6H_4CH_2SH$ $ClCH_2CHOHCH_2Cl$ (3)	$b_{0.3}$ = 143–145	1.5858	80	$C_{10}H_{12}OCl_2S$	47.81	4.78	48.03	4.50
p-$ClC_6H_4SCH_2CHOHCH_2Cl$	*p*-ClC_6H_4SH $ClCH_2CHOHCH_2Cl$ (3)	b_{12} = 193–195	1.5975		$C_9H_{10}OCl_2S$	45.57	4.22	45.88	4.04
p-$ClC_6H_4CH_2SCH_2CHOHCH_3$	*p*-$ClC_6H_4CH_2SH$ $ClCH_2CHOHCH_3$	$b_{0.2}$ = 115	1.5720	94	$C_{10}H_{13}OClS$	55.43	6.00	54.99	5.99
p-$ClC_6H_4CH_2SCCl{=}CHCl$	*p*-$ClC_6H_4CH_2SH$ $Cl_2C{=}CHCl$	b_{14} = 170–172	1.6040	50	$C_9H_7Cl_3S$	42.60	2.76	42.69	2.94
3,4-$Cl_2C_6H_3CH_2SCCl{=}CHCl$	3,4-$Cl_2C_6H_3CH_2SH$ $Cl_2C{=}CHCl$	b_1 = 140–145	1.6147	65	$C_9H_6Cl_4S$	37.50	2.08	37.65	2.38
2,4-$Cl_2C_6H_3CH_2SCCl{=}CHCl$	2,4-$Cl_2C_6H_3CH_2SH$ $Cl_2C{=}CHCl$	$b_{0.5}$ = 120–123	1.6108	65	$C_9H_6Cl_4S$	37.50	2.08	38.73	2.55
2,4-$(CH_3)_2C_6H_3CH_2SCCl{=}CHCl$	2,4-$(CH_3)_2C_6H_3CH_2SH$ $Cl_2C{=}CHCl$	$b_{0.5}$ = 105–108	1.5825	70	$C_{11}H_{12}Cl_2S$	53.44	4.86	53.91	5.26
p-$ClC_6H_4CH_2SCH_2$–(thienyl)	*p*-$ClC_6H_4CH_2SH$ thienyl chloride	b_{11} = 206–207	1.6252	90	$C_{12}H_{11}ClS_2$	56.58	4.32	56.22	4.21
p-ClC_6H_4S–C_6H_9O	*p*-ClC_6H_4SH 2-Chlorocyclohexanone (11)	b_{11} = 200–202	1.5915	80	$C_{12}H_{13}OClS$	59.88	5.40	59.50	5.27
($SCH_2C_6H_4Cl$-*p*, Cl, CH_3, N)	*p*-$ClC_6H_4CH_2SH$ 4,6-dichloroquinaldine	m.p. = 113–114		88	$C_{17}H_{13}NCl_2S$	61.08	3.89	61.70	4.20

TABLE V

PREPARATION OF DISULPHIDES FROM ALKYLENE DIHALIDES AND *p*-CHLOROBENZYL MERCAPTAN OR *p*-CHLOROTHIOPHENOL

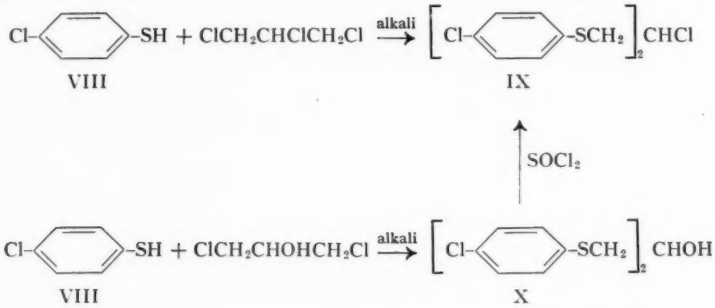
Disulphides prepared R = *p*-ClC_6H_4-	Reactants R = *p*-ClC_6H_4-	M.p.	Yield, %	Empirical formula	Analyses			
					Calc.		Found	
					C	H	C	H
$[RCH_2SCH_2CH{=}]_2$	RCH_2SH and $BrCH_2CH{=}CHCH_2Br$	71–72	87	$C_{18}H_{16}Cl_2S_2$	58.54	4.88	58.55	4.63
$RSCH_2SR$ (9)	RSH and CH_2Cl_2	43–44	85	$C_{13}H_{10}Cl_2S_2$				
$RSCH_2CH_2SR$	RSH and $ClCH_2CH_2Cl$	92–93	32	$C_{14}H_{12}Cl_2S_2$	53.33	3.81	53.31	3.56
$RSCH_2CH_2CH_2SR$	RSH and $ClCH_2CH_2CH_2Cl$	36–37	12	$C_{15}H_{14}Cl_2S_2$	54.71	4.26	54.57	4.19
$RSCH_2CH_2CH_2CH_2SR$	RSH and $Cl(CH_2)_4Cl$	67–68	55	$C_{16}H_{16}Cl_2S_2$	55.98	4.67	55.95	4.61
$RSCH_2CH_2CH_2CH_2CH_2SR$	RSH and $Cl(CH_2)_5Cl$	51–52	35	$C_{17}H_{18}Cl_2S_2$	57.14	5.04	57.23	5.07
$RCH_2SCH_2SCH_2R$	RCH_2SH and CH_2Cl_2	53–54	30	$C_{15}H_{14}Cl_2S_2$	54.71	4.26	54.77	4.21
$RCH_2S(CH_2)_2SCH_2R$	RCH_2SH and $Cl(CH_2)_2Cl$	76–77	32	$C_{16}H_{16}Cl_2S_2$	55.98	4.67	56.02	4.66
$RCH_2S(CH_2)_3SCH_2R$	RCH_2SH and $Cl(CH_2)_3Cl$	23–24	31	$C_{17}H_{18}Cl_2S_2$	57.14	5.04	57.03	4.96
$RCH_2S(CH_2)_4SCH_2R$	RCH_2SH and $Cl(CH_2)_4Cl$	54–55	12	$C_{18}H_{20}Cl_2S_2$	58.22	5.39	58.30	5.45
$RCH_2S(CH_2)_5SCH_2R$	RCH_2SH and $Cl(CH_2)_5Cl$	37–38	18	$C_{19}H_{22}Cl_2S_2$	59.22	5.71	59.06	5.65
$RSCH_2CHOHCH_2SR$	RSH and $ClCH_2CHOHCH_2Cl$	46–47	61	$C_{18}H_{16}OCl_2S_2$	52.18	4.05	51.93	3.81
$RSCH_2CHClCH_2SR$	RSH and $ClCH_2CHClCH_2Cl$	85–86	30	$C_{15}H_{13}Cl_3S_2$	49.53	3.57	49.66	3.45
$RSCH_2COCH_2SR$	RSH and $ClCH_2COCH_2Cl$ (2)	80–81	87	$C_{16}H_{12}OCl_2S_2$	52.48	3.50	52.43	3.45
$RS(CH_2)_3CO(CH_2)_3SR$	RSH and $Cl(CH_2)_3CO(CH_2)_3Cl$ (5)	63–64	80	$C_{19}H_{20}OCl_2S_2$	57.28	5.02	57.45	4.86

peroxide oxidation of the sulphide V, behaved like a typical β-ketosulphone (8) and gave VII in high yield when treated with dilute alkali.



V VI VII

It is interesting to note that 1,2,3-trichloropropane reacted with two moles of *p*-chlorothiophenol to yield 1,3-bis-*p*-chlorophenylmercapto-2-chloropropane (IX) as the main product, and the alkyl chlorine of IX was so inert that it failed to react with potassium thiocyanate, alkali mercaptides, and sodium N,N-dimethyldithiocarbamate. This is surprising in view of the fact that sodium N,N-dimethyldithiocarbamate has been found to react easily with many aliphatic and some aromatic halides (7). That this reaction



VIII IX X

product of VIII and 1,2,3-trichloropropane has the structure IX and is not the 1,2-isomer was indicated by the fact that 1,3-bis-(*p*-chlorophenylmercapto)-2-propanol (X) (obtained from VIII and 1,3-dichloro-2-propanol) could be converted to IX by thionyl chloride.

EXPERIMENTAL

Preparation of 2-Chloroethyl Aryl and Aralkyl Sulphides (Table I)

To a solution of sodium (0.2 mole) in methanol (50 ml.) was added the mercaptan (RSH, R = aralkyl) (0.2 mole). The resulting solution was cooled, ethylene dichloride (300 ml.) was added, and the reaction mixture heated under reflux for ½ hour. The reaction was only slightly exothermic. The reaction mixture containing precipitated sodium chloride was washed with water, the excess ethylene dichloride removed, and the residue distilled. Methanolic potassium hydroxide may be used instead of sodium and methanol with equally good results.

Preparation of the Bis-(aryloxyethyl) and Bis-(arylmercaptoethyl) Sulphides ($RYCH_2CH_2SCH_2CH_2YR$) (XI) from Bis-(2-chloroethyl) Sulphide (Table III)

To a solution of sodium (0.2 mole) in methanol (200 ml.) was added the phenol or the thiophenol (0.2 mole) followed by bis-(2-chloroethyl) sulphide (0.1 mole), and the reaction mixture was heated under reflux for 3 hours. The methanol solution was decanted

from the precipitated salt, the solvent removed, the residue dissolved in benzene, and the benzene solution washed with aqueous sodium hydroxide and with water. The solvent was removed from the benzene solution and the residue crystallized from methanol or benzene.

Preparation of the Sulphides Listed in Table IV

These sulphides were prepared by the same method as were the 2-chloroalkyl aralkyl sulphides (II) of Table I (above) using excess alkyl halide where possible. In those cases where the boiling point of the alkyl halide was over 100° an excess was not used. Instead, benzene or methyl ethyl ketone was employed as solvent. With less reactive halides such as trichloroethylene the reaction time had to be extended to 5 hours.

Preparation of the Disulphides from Alkylene Dihalides (Table V)

The method used here was essentially the same as that employed in the preparation of 1,3-bis-(*p*-chlorophenylmercapto)-2-propanol except that distillation of the final product was not necessary (see p. 526).

p-Chlorobenzyl 2-Chloroethyl Sulphone

To a solution of *p*-chlorobenzyl 2-chloroethyl sulphide (5 g.) (Table I) in acetic acid (15 ml.) was added 30% hydrogen peroxide (15 ml.) and the solution heated on the steam bath for ½ hour with occasional cooling in order to keep the temperature below 100°. The resulting solution was diluted with a few milliliters of water and allowed to cool. White needles (5.4 g. or 95%) precipitated and melted at 119–120°. Anal. calc. for $C_9H_{10}O_2Cl_2S$: C, 42.69; H, 3.96. Found: C, 42.60, 43.17; H, 3.91, 4.11.

p-Chlorobenzyl α,β-Dichlorovinyl Sulphone

This was prepared in poor yield by the above method from *p*-chlorobenzyl α,β-dichlorovinyl sulphide (Table IV), m.p. 70–72°. Anal. calc. for $C_9H_7O_2Cl_3S$: C, 37.83; H, 2.45. Found: C, 37.97, 38.15; H, 2.63, 2.90.

2-p-Chlorobenzenesulphonylcyclohexanone (VI)

This could not be prepared by the above method because the reaction in this case was very exothermic and could not be controlled. To a cold solution of 2-*p*-chlorophenylmercaptocyclohexanone (V) (Table IV) (10 g.) in acetic acid (50 ml.) was added 30% hydrogen peroxide (25 ml.) and the resulting solution was allowed to stand at room temperature for 3 days with occasional cooling on the first day in order to keep the temperature below 30°. The product was worked up as above and when recrystallized from aqueous methanol it melted at 78–80°. The yield was 70%. Anal. calc. for $C_{12}H_{13}O_3ClS$: C, 52.94; H, 4.78. Found: C, 53.25, 53.29; H, 5.07, 4.88.

ω-p-Chlorobenzenesulphonylhexanoic Acid (VII)

To a solution of sodium hydroxide (3 g.) in water (50 ml.) was added 2-*p*-chlorobenzenesulphonylcyclohexanone (1 g.) and the reaction mixture heated on the steam bath for 1 hour. The resulting solution was cooled, acidified with concentrated hydrochloric acid, and the white precipitate (0.80 g. or 78%) filtered, washed, and dried, m.p. 109–110°. It is soluble in aqueous sodium bicarbonate. Anal. calc. for $C_{12}H_{15}O_4ClS$: C, 49.58; H, 5.16. Found: C, 50.00, 49.98; H, 5.22, 5.33.

p-Chlorobenzyl 2-Chloropropyl Sulphide

This was prepared in 90% yield from *p*-chlorobenzyl 2-hydroxypropyl sulphide (Table IV) and thionyl chloride in the usual manner. The colorless liquid boiled at 165°

at 13 mm. pressure, $n_D^{20} = 1.5692$. Anal. calc. for $C_{10}H_{12}Cl_2S$: C, 51.06; H, 5.11. Found: C, 51.29, 51.69; H, 5.07, 5.35.

p-Chlorobenzyl 2,3-Dichloropropyl Sulphide

This was prepared in 90% yield from *p*-chlorobenzyl 2-hydroxy-3-chloropropyl sulphide (Table IV) and thionyl chloride. The colorless liquid boiled at 135–137° at 0.2 mm. pressure, $n_D^{20} = 1.5845$. Anal. calc. for $C_{10}H_{11}Cl_3S_2$: C, 44.53; H, 4.08. Found: C, 44.96; H, 4.29.

p-Chlorobenzyl 2-Thiocyanatopropyl Sulphide

A solution of *p*-chlorobenzyl 2-chloropropyl sulphide (10 g.), sodium thiocyanate (4 g.), and ethanol (75 ml.) was heated under reflux for 2 hours. The ethanol was distilled off, benzene and water were added to the residue, and the whole shaken. The benzene layer was washed, the solvent removed, and the residue distilled, b.p. (0.1 mm.) = 151–153°, yielding 9 g. of colorless liquid, $n_D^{20} = 1.6010$. Anal. calc. for $C_{11}H_{12}NClS_2$: C, 51.26; H, 4.66. Found: C, 51.23; H, 4.76.

1,3-Bis-(p-chlorophenylmercapto)-2-propanol (*X*)

To a solution of potassium hydroxide (24 g.) in methanol (100 ml.) was added *p*-chlorothiophenol (58 g.), benzene (100 ml.), and 1,3-dichloro-2-propanol (26 g.) and the reaction mixture was heated under reflux for 5 hours. Water was then added, the benzene layer separated and washed with water, the solvent removed, and the residue distilled. The fraction boiling at 205–208° at 0.5 mm. pressure was collected and allowed to solidify. It was pulverized, washed with petroleum ether (b.p. 30–60°), and dried. The white powder (42 g. or 61%) melted at 46–47°. Anal. calc. for $C_{15}H_{14}OCl_2S_2$: C, 52.18; H, 4.05. Found: C, 51.90, 51.93; H, 3.86, 3.81.

1,3-Bis-(p-chlorophenylmercapto)-2-chloropropane (*IX*)

A solution of 1,3-bis-(*p*-chlorophenylmercapto)-2-propanol (X) (20 g.), thionyl chloride (20 ml.), and dry benzene (50 ml.) was heated under reflux for 3 hours. The excess thionyl chloride and benzene were removed *in vacuo* and the residue distilled at 195–220° at 0.5–1 mm. pressure. The distillate on crystallization from methanol yielded white needles (13 g. or 60%) which melted at 86–87° alone or in admixture with the product obtained from 1,2,3-trichloropropane and *p*-chlorothiophenol (Table V).

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MECHANISM OF GUANIDINE NITRATION

II. TETRAETHYLNITROGUANIDINE[1]

M. W. KIRKWOOD AND GEORGE F WRIGHT

ABSTRACT

The preparation of *sym*-tetraethylnitroguanidine now shows that a ketimino group can be nitrated directly. The mode of nitration has been evaluated first by determination of the ionization of guanidine bisulphate (prepared anew) and tetraethylguanidine in nearly-anhydrous sulphuric acid by means of an improved cryoscope, and by comparison of these ionizations with those of substances the ionizing behavior of which may be reliably predicted. Subsequent studies show that the stronger base, *sym*-tetraethylguanidine, is nitrated more slowly than guanidine, both reactions being reversible. Detailed kinetic studies were not made because of the irreversible side-reaction yielding tetraethylurea. This irreversible reaction, which is suppressed by sodium bisulphate but not by nitric acid, is presumptive for the existence of an intermediate nitrotetraethylguanidinium salt out of which the tetraethylnitroguanidine or tetraethylurea may arise.

In the first paper of this series (33) it was suggested that nitration of a guanidine occurs at the imino rather than a primary amino nitrogen. In order to test this hypothesis we have examined *sym*-tetraethylguanidine in which only the imino nitrogen is available for replacement of hydrogen by a nitro-group. Nitration does not occur in a nitric acid – acetic anhydride system, but in a nitric acid – sulphuric acid system a 61% yield of *sym*-tetraethylnitroguanidine is obtained. The substance has been characterized by analysis and by alkaline hydrolysis to yield tetraethylurea.

This authentic nitrimine resembles nitroguanidine in many respects. Thus its absorption maximum at 268 mμ is near to that of nitroguanidine (265 mμ), though different from a previous specification of nitrimine absorption (20). The infrared spectra of tetraethylnitroguanidine and nitroguanidine are not comparable because the principal absorption (6.8–7.0 μ) found for the new compound as a supercooled liquid is masked by the mineral oil used for the mull of nitroguanidine (16). However both substances behave similarly by negative Franchimont tests for the nitramine linkage (9). Finally the electric moment of 7.64 D., determined in dioxane at 20°, is higher than that of nitroguanidine (μ = 6.95 D.) (15) by about the contribution that would be expected from the effect of four ethyl groups tetrahedrally disposed at the amino nitrogens. These similarities tend to confirm the nitrimino structure which has been proposed for nitroguanidine (1).

Thus the nitration of tetraethylguanidine seems to resemble that of guanidine, but the rate of nitration is slower. Insofar as imine nitration is thought to resemble secondary amine nitration this result would not be unexpected if tetraethylguanidine were more strongly basic than guanidine (8). Since direct evaluation of electron-donation is of questionable significance in strong sulphuric acid, we have examined instead the extent of salt dissociation by cryoscopic means.

For this cryoscopic evaluation we have prepared the hitherto-unknown guanidine bisulphate, an easily purified anhydrous salt. A salt of tetraethylguanidine satisfactory for cryoscopic study could not be found so the carbonate-free amine was used for the purpose. We have included comparative studies with benzoic acid, trinitrotoluene, dimethylsulphone, and *p*-tolyltrimethylammonium bisulphate. Surprisingly we have

[1]*Manuscript received January 15, 1957.*
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found the latter salt to be satisfactory for cryoscopic studies although Williams and his co-workers (18) reported unworkable hygroscopicity. Possibly they encountered the sulphate salt.

In common with other workers (10, 12) we have found that freezing point determinations in absolute sulphuric acid lead to i values ($\Delta°$ found/$\Delta°$ calc. from molecular weight of solute) which depend on the amount of solute present. Typical is the behavior of benzoic acid, the first item in Table I, using Gillespie's cryoscopic constant (5.98°/g. mole^{-1}. kg.) for absolute sulphuric acid. The freezing point depressions in the first two determinations are smaller than would be expected if benzoic acid dissociates in absolute sulphuric acid according to equation (i):

$$C_6H_5COOH + H_2SO_4 \rightleftarrows C_6H_5CO_2H_2^{\oplus} + HSO_4^{\ominus} \qquad \text{(i)}$$

but the expected result according to equation (i) is obtained (determination 3) when the concentration of solute is increased further.

This behavior has been explained (10, 12) as due to alteration, by the bisulphate ion generated according to equation (i), of the autoprotolysis of sulphuric acid

$$2H_2SO_4 \rightleftarrows H_3SO_4^{\oplus} + HSO_4^{\ominus} \qquad \text{(ii)}$$

ince a shift of (ii) to the left would reduce the particle concentration. According to this explanation the mass effect should decrease with increasing amounts of solute.

The validity of this argument may be questioned, and indeed it has been shown that indiscriminate addition of bisulphate salts leads to ambiguous results (5). Actually the i values for benzoic acid are consistent over a series of concentrations of solute (determinations 4–9 inclusive) when the sulphuric acid is 0.03 molar in water. But this inclusion, which has been thought to contribute sufficient hydronium bisulphate to compensate reaction (ii), causes an apparent dissociation which exceeds that expected of reaction (i). This discrepancy has been evaluated by examination of other substances the dissociations of which are thought to be known.

It has been demonstrated spectroscopically (4) that trinitrotoluene does not react with anhydrous sulphuric acid. We have examined this substance in anhydrous sulphuric acid as well as that containing 0.03 mole per liter of water (determinations 10–21 inclusive, Table I) and find that the i values are essentially the same in both media although they are higher than the expected value of unity. This discrepancy may be due to the use of Gillespie's freezing point constant in a system to which it is not applicable.

A further test of this constant has been made by study of dimethysulphone upon the assumption that it does not undergo salt formation in absolute, or nearly-absolute, sulphuric acid. However the determinations (22–27 inclusive, Table I) do not confirm this assumption. It may be seen that increasing concentration of solute in absolute sulphuric acid causes increasing i values, the maximum of which is about the same as that observed for all solute concentration in sulphuric acid 0.03 molar in water. This might be considered as evidence of partial ionization in the systems.

It was hoped that an examination of trimethyl-*p*-tolylammonium bisulphate would specify the freezing point constant since this quaternary ammonium salt might be expected to be so completely dissociated in sulphuric acid that the system would be characterized by an i value of 2. This hope has not been realized. Determinations 28–30 inclusive (Table I) show increasing i values with increasing concentration despite the use of a sulphuric acid which is not anhydrous. Furthermore the maximum i value,

TABLE I

DEPRESSIONS OF THE FREEZING POINT OF SULPHURIC ACID CAUSED BY SUCCESSIVE ADDITIONS OF SOLUTE

Solute			Sulphuric acid				
Name	Wt., g.	F.P. No.	Wt., g.	Molal content of water	Δ° C. found	Δ° C. calc.	"i" value
Benzoic acid	.0471	1	29.30	Nil	.140	.078	1.74
	.0872	2	„	Nil	.269	.145	1.85
	.1295	3	„	Nil	.433	.216	2.00
	.0361	4	28.66	.03	.140	.062	2.26
	.0968	5	„	.03	.352	.166	2.12
	.1345	6	„	.03	.482	.230	2.10
	.0315	7	31.30	.03	.103	.049	2.11
	.0802	8	„	.03	.272	.216	2.16
	.1472	9	„	.03	.482	.231	2.09
Trinitrotoluene	.0371	10	29.67	Nil	.079	.065	1.21
	.1586	11	„	Nil	.164	.141	1.16
	.2331	12	„	Nil	.233	.207	1.13
	.0633	13	33.22	Nil	.057	.050	1.14
	.1417	14	„	Nil	.129	.112	1.15
	.2230	15	„	Nil	.206	.178	1.16
	.0671	16	31.07	.02	.065	.057	1.14
	.1298	17	„	.02	.124	.110	1.13
	.2090	18	„	.02	.209	.178	1.17
	.0582	19	34.26	.03	.053	.045	1.17
	.1187	20	„	.03	.105	.091	1.15
	.1930	21	„	.03	.171	.149	1.15
Dimethylsulphone	.0278	22	29.77	Nil	.065	.060	1.03
	.0610	23	„	Nil	.147	.131	1.12
	.1072	24	„	Nil	.271	.229	1.18
	.0361	25	31.89	.03	.084	.072	1.17
	.0717	26	„	.03	.168	.143	1.18
	.1050	27	„	.03	.251	.210	1.19
Trimethyl-*p*-tolyl-ammonium bisulphate	.0923	28	30.09	.03	.142	.074	1.92
	.1462	29	„	.03	.234	.118	1.98
	.2354	30	„	.03	.403	.189	2.13
Guanidine bisulphate	.0892	31	31.41	Nil	.136	.108	1.26
	.1714	32	„	Nil	.352	.208	1.69
	.2380	33	„	Nil	.550	.288	1.91
	.3225	34	„	Nil	.799	.391	2.04
	.0841	35	29.51	.03	.265	.109	2.43
	.1706	36	„	.03	.528	.220	2.40
	.2219	37	„	.03	.704	.286	2.46
	.3078	38	„	.03	.966	.396	2.44
sym-Tetraethylguanidine	.0416	39	29.72	.03	.149	.049	3.04
	.0902	40	„	.03	.316	.107	2.95
	.1378	41	„	.03	.497	.162	3.07
	.0355	42	34.37	.03	.117	.036	3.24
	.0742	43	„	.03	.229	.076	3.02
	.1230	44	„	.03	.367	.126	2.92

2.13, exceeds the theoretical value of 2 by approximately the same discrepancy that has been observed for the three other test substances which were examined. This (so-called) discrepancy cannot be a function of time, at least for determination 30, Table I, because the difference (10.308° − 9.905°) was reproducible within 0.001° 12 hours after the original measurement.

In view of these results we are inclined to agree with Wyatt (34), and indeed to extend his opinion to electrolytes, that the cryoscopic method is inaccurate as an evaluation

of basic strength. Nevertheless comparison with the same type of substance ought to be qualitatively valid, and this we have done with guanidine and tetraethylguanidine.

Upon the basis of freezing point lowering caused by guanidine carbonate in absolute sulphuric acid Hantzsch and Geidel (13) considered this amidine to be triprotonated. However, decomposition of the carbonate added an equivalent of water so that the medium was about 0.03 molar in water. Recalculation of Hantzsch's data with use of Gillespie's cryoscopic constant reduces the i value to about 2.8.

Other workers (31) have studied the behavior of the benzoate, perchlorate, and benzenesulphonate of guanidine in sulphuric acid about 0.03 molar in water and have arrived at an i value of about 2.4. It may be seen (determinations 35–38 inclusive, Table I) that our values obtained from guanidine bisulphate in nearly-anhydrous sulphuric acid are in agreement. In absolute sulphuric acid we observe the same i value increase with increasing concentration which is characteristic of the other solutes that we and others have examined.

TABLE II

INTERCONVERSION OF *sym*-TETRAETHYLGUANIDINE (STEG) AND TETRAETHYLNITROGUANIDINE (STENG) IN SULPHURIC ACID SUBSTRATE AT 0°

Expt.	Wt.% H_2O in substrate	Mole ratio $\frac{HNO_3}{STEG}$	Time, hr.	Analyses, mole/l. STEG	Analyses, mole/l. STENG	% STEG accounted for
1	5	5.06	0	.341	0	—
			0.25	.205	.120	95
			0.75	.141	.175	93
			1.0	.119	.192	91
			1.5	.091	.216	90
			2.0	.067	.235	89
			5.0	.020	.274	86
			10.0	.012	.265	81
			24.0	.012	.231	71
2	5	1.14	0	.353	0	—
			0.5	.329	.019	99
			1.5	.370	.029	95
			3.5	.288	.044	94
			6.5	.266	.062	93
			11.5	.256	.074	92
			26.5	.234	.080	89
3	8.8	5.86	0	.290	0	—
			0.16	.164	.119	98
			0.40	.118	.147	91
			0.66	.097	.170	92
			1.16	.058	.200	89
			2.00	.031	.232	91
			4.00	.0082	.246	88
			6.0	.0045	.246	86
			8.0	.0046	.242	85
			20.0	.0044	.209	73
4	8.8	1.35	0	.311	0	—
			0.33	.263	.035	96
			1.33	.223	.064	92
			5.00	.156	.129	92
			10.0	.089	.183	87
			23.0	.052	.210	84
5	16.2	5.18	0	.361	0	—
			0.16	.323	.020	95
			0.50	.295	.038	92
			1.5	.245	.089	93

TABLE II—*concluded*

INTERCONVERSION OF *sym*-TETRAETHYLGUANIDINE (STEG) AND TETRAETHYLNITROGUANIDINE (STENG) IN SULPHURIC ACID SUBSTRATE AT 0°

Expt.	Wt.% H_2O in substrate	Mole ratio $\frac{HNO_3}{STEG}$	Time, hr.	Analyses, mole/l. STEG	Analyses, mole/l. STENG	% STEG accounted for
			3.5	.165	.157	89
			5.5	.118	.208	90
			8.5	.071	.246	88
			23.5	.015	.299	87
			33.5	.009	.300	86
6	16.2	1.45	0	.340	0	—
			2.25	.286	.030	93
			8.25	.222	.088	91
			25.2	.126	.163	85
			35.3	.091	.171	77
7	5		0	0	.244	—
			0.25	.017	.208	92
			0.4	.026	.197	91
			0.66	.025	.190	88
			1.0	.038	.181	90
			2.16	.059	.155	88
			4.25	.095	.116	86
			7.0	.101	.082	75
			24.0	.144	.024	69
			53.0	.145	.019	67
8	8.8	∞	0	0	.171	—
			0.5	.004	.151	91
			2.0	.006	.147	90
			5.0	.012	.135	87
			10.0	.020	.124	84
			21.5	.033	.094	74
			34.0	.035	.081	68
			46.0	.038	.075	66
9	16.2	∞	0	0	1.70	—
			0.5	0	1.56	91
			1.0	0	1.58	93
			2.0	0	1.56	91
			4.0	0	1.56	91
			8.0	.0007	1.55	91
			25.0	.0030	1.52	91
			54.0	.0051	1.48	90
10	8.8	Footnote A	0	0	.170	—
			0.5	.0017	.158	94
			2.0	.0021	.151	90
			4.5	.0025	.145	87
			9.5	.0025	.137	82
			21.0	.0021	.129	77
			34.0	.0019	.117	70
			46.0	.0020	.101	61
11	8.8	Footnote B	0	0	.170	—
			0.5	.0071	.147	91
			1.5	.0117	.142	91
			4.5	.0301	.120	88
			9.5	.0453	.103	87
			24.0	.0666	.079	86
			34.0	.0748	.062	81
			53.0	.0794	.055	79

(*A*) *Nitric acid added to give mole ratio of* $HNO_3/STENG$ *equal to 5.25.*
(*B*) *Sodium bisulphate added to give mole ratio of* $NaHSO_4/STENG$ *equal to 4.20.*

We would have preferred to examine *sym*-tetraethylguanidine exactly like guanidine but we were unable to prepare a sulphate salt of the tetraethyl homologue which was sufficiently non-hygroscopic for freezing point determination. However the base itself was amenable to use in nearly-anhydrous sulphuric acid. As Table I (determinations 39–44 inclusive) shows, the compound is a stronger proton acceptor than guanidine in sulphuric acid, in conformity with its lesser rate of nitration.

Similarly with guanidine (28, 32) the nitration of tetraethylguanidine is reversible. Solutions of 0.09 g. of the nitro compound in 1 g. of 96.6% and 95.0% sulphuric acids after 60 minutes gave precipitates of nitron nitrate equivalent to 12.6% and 1.7% of denitration respectively. On the other hand no nitron nitrate could be detected after 60 minutes in 92.8% sulphuric acid. The denitration is thus critically dependent on the alteration of the system by water.

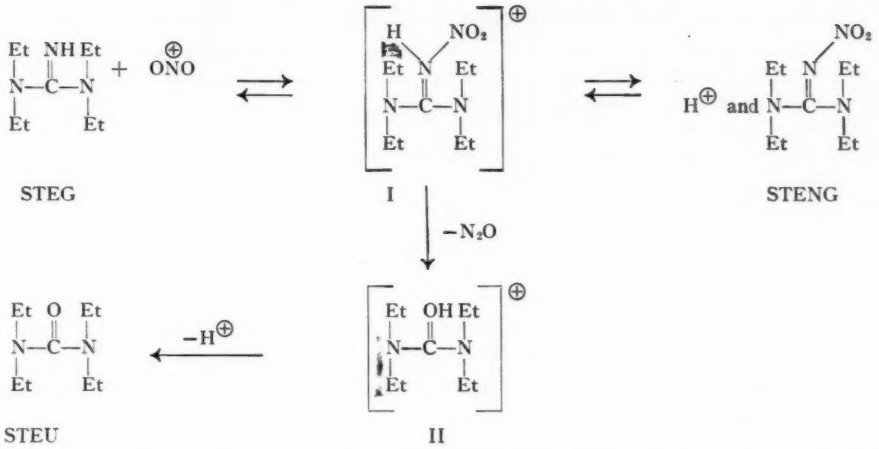
A detailed study of the nitration of *sym*-tetraethylguanidine (STEG) and the denitration of *sym*-tetraethylnitroguanidine (STENG) has been accomplished by separation of STEG and STENG from the reaction system by means of ion-exchange resins with subsequent evaluation of each by ultraviolet absorption intensities. Comparative reactions have been carried out in 95%, 91.2%, and 83.8% sulphuric acid.

The data of Expts. 2, 4, and 6, Table II, in which a ratio of nitric acid to STEG slightly greater than 1 is maintained, show that the maximum reaction rate occurs when the water content of the medium is about 10–15%. This phenomenon has been observed in the nitration of amides (27), amidines like guanidine (26), and aromatic nitro-compounds (19, 3, 30). Since the rate maximum is approximately the same for nitration of these several types it is evident that the behavior is principally a function of the properties of the sulphuric acid medium. An adequate explanation, which has not yet been forthcoming, must await a new insight into the nature of this common, yet little-understood, substance called sulphuric acid.

Inspection of Expts. 1 and 3 (less apparent, 5) shows that the yield of tetraethylnitroguanidine (STENG) with respect to time is only temporarily maximal. This evidence of a side reaction, indicated also by the per cent of tetraethylguanidine (STEG) not accounted for by the analytical method, has been confirmed by examination of a system in 95% sulphuric acid which was allowed to proceed to completion. The identification of tetraethylurea and nitrous oxide shows that this side reaction is an irreversible decomposition of the desired product, STENG, and the kinetic data show that this decomposition is faster in stronger sulphuric acid.

This irreversible decomposition has been confirmed by treatment of the desired nitration product, STENG, with aqueous sulphuric acid containing 95, 91.2, and 83.8% of the acid. Experiments 7, 8, and 9 show that the rapid reversible denitration reaction is followed by a slower irreversible reaction which must be the decomposition of *sym*-tetraethylnitroguanidine (STENG) to tetraethylurea and nitrous oxide. It is shown (Expt. 10) that this irreversible decomposition is not affected appreciably by excess of nitric acid, although, as might be expected, the nitric acid represses the reversible denitration. On the other hand it is of interest to note that the addition of sodium bisulphite (Expt. 11) has little effect on the reversible denitration but it retards profoundly the irreversible decomposition in which tetraethylguanidine disappears from the system.

Assuming that this bisulphate salt operates by protonic capture, one may formulate the following reaction series to explain these phenomena:



According to this concept, nitration proceeds by coordination of nitronium ion with STEG to give the ammononitronium ion I. This ion may be converted reversibly to either STEG, the tetraethylguanidine, or else the nitration product STENG with loss of a proton. An excess of nitric acid forces the equilibrium from STEG to STENG without decreasing the concentration of the intermediate ion I whereas sodium bisulphate, by inactivation of both nitronium and hydrogen ion (or its solvated equivalent), reduces the concentration of I. But the complex ion I may also decompose irreversibly by loss of nitrous oxide to yield ephemerally the tetraethylisourea cation II which, by loss of hydrogen ion or its equivalent, appears as *sym*-tetraethylurea, STEU.

Such a concept has been shown to be untenable in the instance of, say, toluene nitration (21, 2), where the absence of an isotope effect precludes an equilibrium between complex nitronium ion and product, which would be shifted by presence of bisulphate ion. However the difference in coordinative power between toluene and tetraethylguanidine is profound, and a significant concentration of ammononitronium ion I is not unexpected. In the present instance it is of interest to examine a nitratable compound, the cation acceptance of which is intermediate between STEG and toluene.

The nitration of guanidine, which falls into this category, has been studied by Williams and Simkins (32). There is no detectable tendency in this reaction to form the urea as a by-product, at least at the lowest temperature (15°) which these workers employed. In order to establish a basis for comparison with tetraethylguanidine we have nitrated guanidine (as the carbonate) at 0° in sulphuric acid initially containing 16.2% of water (see Table III). We find that the reaction is almost complete within 5 minutes, and no decomposition of the product occurs. Comparison of this nitration rate with that of tetraethylnitroguanidine under the same conditions (Table II) shows that nitroguanidine is formed about 700 times as fast as its tetraethyl homologue. Since the nucleophilicity

TABLE III

NITRATION OF GUANIDINE IN 83.8% SULPHURIC ACID AT 0°
Initial moles guanidine carbonate: moles HNO_3 = 0.411 mole/liter: 0.569 = 1.38

Time, min.	5	20	60	240	600
Conc. nitroguanidine, moles/l.	0.378	0.389	0.401	0.378	0.389

of guanidine is less than that of tetraethylguanidine (STEG, Table I) it would seem that the nitration rate was dependent on a balance between acquirement of alternative ions, exemplified in the formulation above as nitronium and hydrogen ions. Essentially this is the behavior of secondary amines with respect to nitration, thus justifying a formal relationship between R_2NH and R_2CNH (6, 8).

We believe that the general tendency of the nitroguanidines toward decomposition into nitrous oxide and the analogous ureas also supports the concept of the intermediacy of complex nitronium salts during nitration of amines. Although nitroguanidine itself does not undergo this decomposition in the acid reaction media at 25° (32) it is unstable in this respect at higher temperatures (14). This decomposition might have occurred via a primary nitramino group in nitroguanidine but this path obviously is impossible for *sym*-tetraethylnitroguanidine. Insofar as the two guanidines are analogous the nitration may be considered to operate through a complex cation such as I, which ought to behave toward excess nitric acid and toward sodium bisulphate in the manner which we observed during nitration of STEG.

EXPERIMENTAL*

sym-Tetraethylnitroguanidine, STENG

To a solution of 1.71 g. (0.01 mole) of *sym*-tetraethylguanidine (24, the final Grignard reaction should stand for 10 hours prior to hydrolysis) in 14.7 g. (0.15 mole) of 100% sulphuric acid at 0° C. was added with stirring over a period of 20 minutes, 3.15 g. (0.05 mole) of 99.9% nitric acid. The colorless reaction system was maintained at 0° C. for 60 minutes and then was dripped slowly onto 25 g. of crushed ice. The drowned reaction system was then neutralized by addition of solid sodium carbonate and the amber oil which separated was collected by three 25-ml. extractions with chloroform. The combined extract, dried by magnesium sulphate, was distilled, first at 25° C. (20 mm., 1.65 g.), and then at 0.01 mm., to yield 0.01 g., b.p. 55° C. (identified as tetraethylurea by conversion to its chloroplatinate), and then 1.33 g. (61%), b.p. 141–142° C., solid at 30° C. Low temperature crystallization from ethyl acetate gave a melting point of 37.3–38.0° C. Calc. for $C_9H_{20}O_2N_4$: C, 50.0; H, 9.32; N, 25.9. Found: C, 49.8; H, 9.07; N, 26.0. The substance showed an absorption band at 268 mμ (molar extinction coefficient, 1.195×10^4) as contrasted to tetraethylguanidine with a band at 227 mμ where the nitro compound again absorbed strongly. The infrared spectrum is recorded in μ at K_e, 2.95 [0.921], 3.35 [6.12], 3.45 [6.10], 6.50 [1.171], 6.68 [0.968], 6.85 [1.302], 6.95 [1.378], 7.25 [0.798], 7.48 [0.635], 7.67 [0.783], 7.80 [0.916], 8.05 [2.931], 8.75 [0.744], 8.90 [0.724], 9.05 [0.761], 9.26 [0.798], 9.85 [0.607], 10.10 [0.654], 10.50 [0.519], 10.60 [0.548], 10.75 [0.611], 12.10 [0.394], 12.45 [0.494], 12.65 [0.536], 12.85 [0.494], 13.40 [0.616], 13.50 [0.629]. The electric moment in dioxane at 500 kc. at 200° C. is 7.64 D., calculated by the method of Halverstadt and Kumler (11); P (total) = 1290 cc.; MR_D calc.: 61.1 cc., found from n_D^{20} 1.51880 and d_4^{20} 1.037 using supercooled liquid: 63.2. However, if the atomic polarization determined for nitroguanidine from the dielectric constant of solid pellets (22) at maximum density ($P_a = P_{e+a} - MR_D = 30.4 - 23.2 = 7.2$ cc.) applies to the tetraethyl analogue, then μ for STENG = 7.61 D. STENG does not give a true Franchimont test for secondary nitramines although a green color develops on the zinc surface in diethylaniline – acetic acid. The X-ray diffraction pattern, determined with Cu K_α radiation (Ni filtered), is reported as intensities [I/I_1] at spacings

Melting points have been corrected against reliable standards (Can. J. Technol. **34, 89 (1956)).*

in Ångstroms: [10] 4.84; [9] 8.11; [7] 3.95; [6] 7.02, 3.80; [5] 8.75, 5.50, 3.56, 3.50; [4] 5.77, 3.18, 2.92; [2] 2.62, 2.49; [1] 4.36, 4.10, 3.03, 2.39.

Tetraethylurea

a. By Decomposition of Tetraethylnitroguanidine in Alkali

A mixture of 0.50 g. (0.0025 mole) of tetraethylnitroguanidine and 5 ml. of 20% aqueous sodium hydroxide (0.025 mole) was heated under reflux for 150 minutes. The cooled two-phase system was twice extracted with chloroform and the 20 ml. of extract, dried with magnesium sulphate; was vacuum-evaporated. The residue (0.31 g.) was distilled, b.p. 90–91° C. (9 mm.), 0.16 g. (40%); the chloroplatinate did not depress the melting point of an authentic sample.

b. By Decomposition in 96% Sulphuric Acid

A mixture of 0.669 g. (0.0031 mole) of tetraethylnitroguanidine and 5 ml. of 96% sulphuric acid was stirred magnetically at 20° C. for 1 day while the evolved gas was collected over water. By combustion with hydrogen this gas was found to contain 18.4 cc. of nitrous oxide (27%). The remaining liquid was poured onto ice and diluted to 100 ml. with water. Threefold extraction with ether followed by processing as described above gave a 51% yield of authentic tetraethylurea.

c. From Diethylamine and Phosgene

This product, prepared by the method of Michler (23), did not give the chloroplatinate (m.p. 134° C. but not analyzed) reported previously (25) but instead a chloroplatinate with m.p. 98–99° C. Calc. for $(C_9H_{20}N_2O)_2H_2PtCl_6$: Pt, 25.9. Found: Pt, 26.6.

Guanidine Bisulphate

To 13 ml. (0.25 mole) of 100% sulphuric acid in a flask protected from air was added in small quantities 15.1 g. (0.08 mole) of guanidine carbonate. Upon cooling to 20° C. the system became a white slush which was triturated seven times with 100-ml. volumes of diethyl ether in order to remove the excess sulphuric acid. Subsequently the ether-insoluble portion was filtered off and dried to constant weight *in vacuo*, 23.6 g. (89%), m.p. 101.0–101.5° C. after two crystallizations from hot acetic acid. Calc. for $CH_7O_4N_3S$: N, 26.7; SO_4, 61.1. Found: N, 26.2; SO_4, 60.9. The picrate prepared from this salt melted at 325–330° C.; admixture with authentic guanidine picrate did not depress this melting point.

p-Tolyltrimethylammonium Bisulphate

A solution of 15.0 g. (0.054 mole) of *p*-tolyltrimethylammonium iodide (prepared from *p*-dimethyltoluidine and methyl iodide in anhydrous diethyl ether) in 200 ml. of 95% ethanol was treated with small quantities of freshly-precipitated silver oxide until the formation of silver iodide was no longer evident. The silver salts were then filtered off and washed well with 95% ethanol. Filtrate and washings, combined, were chilled to 0° C. Then 96% sulphuric acid was added slowly until the pH of the system reached about 2. After vacuum evaporation of the solvent the amber gummy solid was redissolved in 125 ml. of absolute ethanol and this solution was decolorized by Norit. Subsequent addition of 150–200 ml. of absolute diethyl ether gave 9.61 g. (72%) of white leaflets, m.p. 133–136° C. This crude bisulphate was purified by solution in absolute ethanol followed by precipitation with absolute ether, m.p. 132.5–133.3° C. Calc. for $C_{10}H_{17}O_4NS$:

SO_4, 38.9. Found: SO_4, 38.9. The melting point of the picrate prepared from this salt (m.p. 197–198° C.) was not depressed by admixture with an authentic sample (29).

Dimethyl Sulphone

This substance, prepared by hydrogen peroxide oxidation of dimethyl sulphide (7), was dissolved in 80 ml. of saturated aqueous sodium sulphate and this solution was continuously extracted with chloroform. The extract, dried over sodium sulphate, was vacuum-evaporated and the 3.1 g. (47%), m.p. 107–110° C., was twice crystallized from hot chloroform (10 ml. per g.), m.p. 109.3–110.0° C. (soft 108.5° C.). The literature reports a melting point of 109° C. (17).

Analytical Procedure for Kinetic Studies

In order to separate tetraethylguanidine and tetraethylnitroguanidine from nitric and sulphuric acids, and from each other, the drowned aliquots were passed through a 15×2 cm. column containing Amberlite IR-4-B ion exchange resin (Dowex-2 was too basic and destroyed the nitration product) to retain as much of the mineral acids as possible. Thence the eluate was passed through a column 2 cm. by 0.8 cm. containing Dowex-50 in order to remove tetraethylguanidine. Since this base is stronger than the IR-4-B resin, the eluate from the Dowex-50 contained some sulphuric acid which was subsequently removed by a third column, 5 cm. by 1.5 cm., containing IR-4-B.

The eluate from the three tandem columns contained only tetraethylnitroguanidine. The amount was ascertained by comparison of the absorption spectrum with those of standard solutions via identical columns (see Table IV).

TABLE IV

DETERMINATION OF MOLAR EXTINCTION COEFFICIENT AT 268 mμ OF *sym*-TETRAETHYLNITROGUANIDINE IN AQUEOUS SOLUTION

Conc., mole/l. × 10^{-5}	1.027	2.054	3.081	4.108	5.135	6.162	7.189
Molar extinction coefficient × 10^4	1.199	1.207	1.198	1.184	1.197	1.188	1.213

The tetraethylguanidine was recovered by inverting the Dowex-50 column and washing it with 4 *N* sulphuric acid. The eluted salt in aqueous acid was evaluated by comparison of the absorption spectrum with those of standardized solutions via identical columns (see Table V).

TABLE V

DETERMINATION OF MOLAR EXTINCTION COEFFICIENT AT 227 mμ OF *sym*-TETRAETHYLGUANIDINE IN 4 *N* SULPHURIC ACID

Conc., mole/l. × 10^{-5}	1.43	2.86	4.29	5.72
Molar extinction coefficient × 10^3	9.16	9.19	9.12	9.13

Mixtures of known composition comprising the two compounds were found to be 96–100% recoverable according to spectroscopic analysis, while the presence of tetraethylurea interfered neither with the separation nor with the subsequent spectrometry since the urea is transparent in the spectral regions involved in the analysis.

Kinetic Procedure

The nitration of *sym*-tetraethylguanidine in sulphuric acid, and the subsequent analyses, were carried out as follows. A weighed quantity of tetraethylguanidine was added to the appropriate medium containing sulphuric acid. A solution of absolute

nitric acid in sulphuric acid of the same strength was prepared at 0° C. and the two solutions were mixed at 0° C. and made up rapidly to a volume of 10 ml. by addition of more of the sulphuric acid medium, then shaken rapidly at 0° C. for 1 minute and thereafter maintained at this temperature. Periodically 1-ml. samples were withdrawn and drowned on 20–25 g. of ice. These aliquots were made up to 100-ml. volumes with distilled water and then were passed successively through the ion-exchange columns. Subsequently the three tandem columns were washed with 350 ml. of water. The combined eluates were made up to a 500-ml. volume with distilled water and then diluted appropriately (usually 2 ml. to 25 ml.) for optical density determination at 268 mμ to indicate the amount of tetraethylnitroguanidine.

The Dowex-50 columns were inverted and eluted with 250 ml. of 4 *N* sulphuric acid. The eluates, made up to 300 ml. with the same acid and usually diluted (2 ml. to 25 ml.), also with 4 *N* sulphuric acid, were examined for optical density at 227 mμ for the amount of tetraethylguanidine.

Nitration of Guanidine

A solution of guanidine carbonate in sulphuric acid of known concentration was prepared at 0° C. To this solution was added a solution of 99.9% nitric acid in sulphuric acid of the same known concentration and the whole at 0° C. was made up quickly to 10 ml. with this sulphuric acid. Periodically 1-ml. aliquots were drowned on 20–25 g. of ice, then diluted to about 100 ml. with distilled water and passed through a 15×2 cm. column of Amberlite IR-4-B resin. This column was washed with water until the combined eluates equalled 500 ml., of which 2 ml. diluted to 25 ml. was usually used for optical density measurement at 264 mμ, where guanidine is transparent. The molar extinction coefficient of nitroguanidine at this wavelength was determined with solutions of concentration 5.30, 2.65, and 7.95×10^{-5} mole/liter as 1.56, 1.54, 1.55×10^{4}, or an average of 1.55×10^{4}. Similar solutions of known concentration were passed through the IR-4-B columns to prove by optical density measurement that recoveries of 98.7–99.6% were effected.

Cryoscopy in Sulphuric Acid

A. The Cryostat

In the apparatus shown in Fig. 1 the stainless-steel stirrer is driven by a cam which is rotated by a variable-speed motor. The temperature is measured by means of a Western Electric Type 14-A thermistor (*R* at 0° C. 3.5×10^{5} ohms, at 50° C. 3.5×10^{4} ohms), which is a part of the Wheatstone bridge shown in Fig. 2. Calibration with respect to a U.S. Bureau of Standards thermometer by plotting the logarithm of resistance of the variable arm of the bridge against the reciprocal of absolute temperature at the thermistor shows that the variation is linear and sensitive to 0.001° C.

For operation, the Wheatstone bridge is balanced at approximately 9° C. by adjustment of the variable resistance arm with respect to the galvanometer and then is switched to the Leeds and Northrup Speedomax recorder, the chart paper width of which covers a temperature range of about 0.35° C., thus facilitating readings to at least 0.001° C. In order to cover the range 9.0–10.4° C. four range settings are necessary, and these are available by means of the variable resistance arm of the bridge, which is adjusted to return the recorder pen to the origin at each step. In practice the recorder is connected when a deflection on the table galvanometer shows that solidification is commencing.

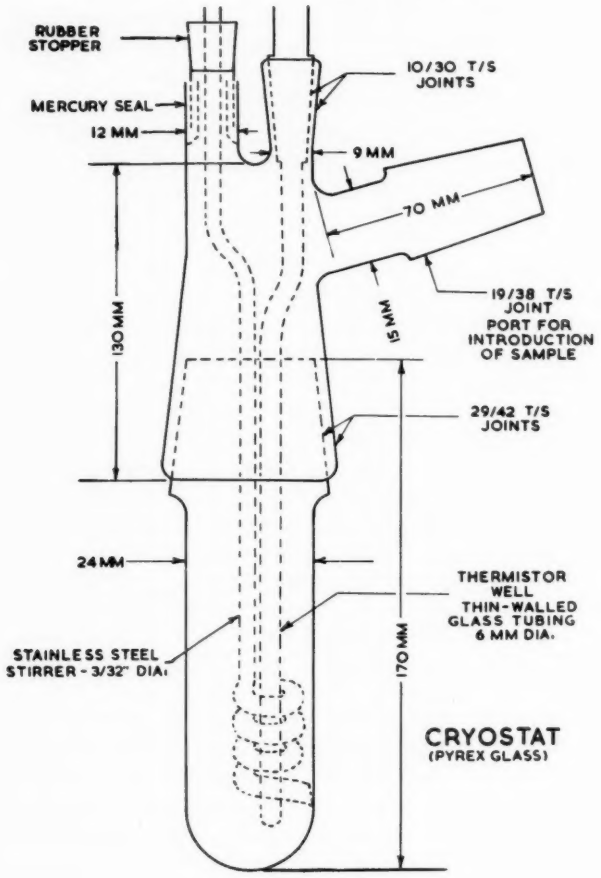


FIG. 1.

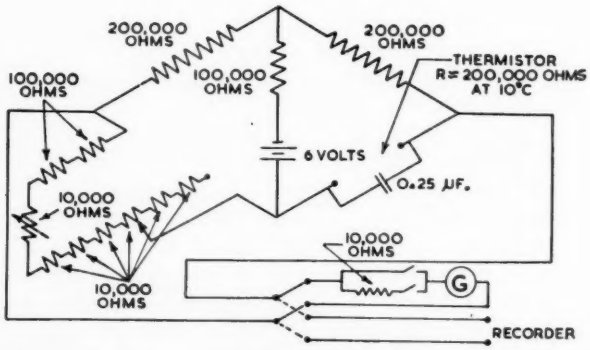


FIG. 2. Electrical circuit for measuring temperature changes in cryostat No. 2.

B. Procedure

Between 25 and 35 g. of absolute sulphuric acid is pipetted into the lower extremity of the cryostat, which previously has been flamed during passage of dry nitrogen through it. An air jacket with an inlet tube is then fitted around the lower extremity of the cryostat and the assembly is immersed in a bath of crushed ice. The sulphuric acid is then stirred under a slight positive pressure of nitrogen at the rate of 90 to 95 strokes per minute of the stainless-steel stirrer (Fig. 1). It is essential to the success of the experiment that the lowest extremity of the stirrer scrapes the wall of the cryostat during the entire stroke.

When the temperature of the sulphuric acid is about 2° C. above the freezing point a piece of dry ice (2 cm. by 0.5 cm. by 0.5 cm.) is passed along the lateral inlet tube of the air jacket and is pressed against the wall of the cryostat for 45 seconds. The seeds of sulphuric acid which form on the interior wall are dispersed through the medium by the action of the stirrer as it scrapes along the wall of the cryostat. In this manner supercooling of anhydrous sulphuric acid is avoided entirely and a time–temperature cooling curve is obtained without the necessity for corrections (10).

The solute, weighed into a very-thin-walled glass tube, is introduced into the cryostat through the 19/38 joint (Fig. 1) and is crushed manually against the wall of the cryostat with the aid of the stirrer in order to ensure uniform distribution throughout the cryoscopic medium. The freezing point is then determined from the chart record by reference to the calibration curve for the thermistor used in the bridge circuit. The results are reproducible to at least 0.003° C. if, and only if, current has been passed through the thermistor for about 12 hours prior to the determination.

ACKNOWLEDGMENTS

The authors are grateful to Messrs. Myers and Bedard of the Defence Research Board for the infrared spectrum and to Mrs. Liselotte Westland for the dipole moment determination. Also they are grateful to the Defence Research Board and the National Research Council for financial aid in support of this investigation.

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ION-EXCHANGE METHODS FOR THE QUANTITATIVE SEPARATION OF THE ALKALINE EARTHS, AND THEIR APPLICATION TO THE DETERMINATION OF Sr^{90} IN MILK ASH[1]

GWEN M. MILTON AND W. E. GRUMMITT

ABSTRACT

A study has been made of the effects of column loading and eluting agent on the cation-exchange separation of the alkaline earths—beryllium, magnesium, calcium, strontium, barium, and radium. The principal eluting agents tested were ammonium lactate, ammonium citrate, and hydrochloric acid. Dowex-50 resin (Ion X, 300–400 mesh) was used throughout the investigation, and the column temperature was maintained at approximately 80° C. Under optimum conditions, involving the use of 0.25 g. of resin per milliequivalent of sample and with ammonium lactate eluant (0.55 *M* at pH 5 for beryllium, and 1.5 *M* at pH 7 for magnesium, calcium, strontium, barium, and radium), a quantitative separation of all six elements in a single sample is possible in 5 hours. This procedure has been applied to the routine analysis of Sr^{90} in bulk milk ash samples, containing 20 mg. of strontium carrier, with yields of 85–95%. By the same method trace amounts of strontium naturally occurring in milk have also been determined.

INTRODUCTION

In recent years many investigators have reported separations of neighboring pairs of alkaline earths by methods other than precipitation procedures, e.g. paper chromatography (6, 11), anion-exchange (13), and numerous cation-exchange procedures utilizing such eluting agents as ammonium citrate (15), ammonium lactate (10), ammonium acetate (8), ethylenediamine tetraacetic acid (1, 4), and hydrochloric acid (2, 3). The cation-exchange method has been used almost exclusively in the few papers which have reported quantitative data (2, 10), and this technique would appear to be the most promising one for quantitatively separating millimoles of alkaline earth phosphates.

An estimation of the degree of separation obtained between two elements can be made by calculating the ratio of their distribution coefficients (D = milliliters of eluate to peak less one interstitial column volume/weight of resin in grams (12)). Using 1.2 *M* ammonium lactate eluant at room temperature, Lerner and Rieman (10) obtained the ratios Sr/Ca = 1.5, Ba/Sr = 2.5, and although millimole quantities of strontium and calcium were quantitatively recovered under these conditions, a greater separation would seem desirable for rapid or routine analysis. Campbell and Kenner (2) obtained data which give a ratio of distribution coefficients $Ca/Mg > 3$, using 1.07 *M* and 1.21 *M* hydrochloric acid eluant, also at room temperature. No mention was made of extending this method to include strontium and barium separations, but a recent study by Diamond (3) of alkaline earth distribution factors in hyrochloric acid indicated the feasibility of good separations between these two elements.

The purpose of this investigation was to determine whether milligram quantities of beryllium, magnesium, calcium, strontium, barium, and trace amounts of radium could be recovered quantitatively from a single sample in a few hours, and, by a study of various eluting agents at elevated temperature and the effects of column loading, to determine the optimum conditions for such a separation.

Following this work a severe test of the flexibility of the separation using 1.5 *M* ammonium lactate eluant was made by applying it to the analysis of milk and bone

[1]*Manuscript received November 14, 1956.*
Contribution from Research Chemistry Branch, Atomic Energy of Canada Limited, Chalk River, Ontario. Issued as A.E.C.L. No. 441.

ash. Ion-exchange techniques have previously been used to determine the alkali metals in these substances (14, 5); in this paper the new data were applied to the analysis for other constituents in the following two cases: (*a*) the recovery of calcium-free strontium, barium, and radium from bulk samples (15–17 g.) containing 2.5 g. (approx.) of calcium, and 20 mg. of added strontium, in order to measure Sr^{90} levels in milk routinely; (*b*) the determination of 70–130 p.p.m. of strontium in samples containing 16% of calcium (the composition of the average milk ash).

EXPERIMENTAL

The column used for most of the separations was a 1.1 cm. i.d. by 10 cm. long sinter funnel, packed with Dowex-50 (Ion X, 300–400 mesh) to a height of 8 cm. above the sinter. In addition two other sizes were employed; a 1.0 cm. i.d. by 2.0 cm. bed was used for some of the barium–radium separations to obtain smaller elution volumes and a 2.8 cm. i.d. by 10 cm. column, packed to a height of 9 cm. with approximately seven times the weight of resin in the original column, was required for the larger milk ash samples (15 g.).

Although improved separations are obtained at elevated temperatures in most instances (9), the operation of a column at 80–100° C. is not universal because of the complexity of the apparatus required and the associated troubles arising from the release of gas in the resin. Both of these objections have been satisfactorily overcome by the method adopted here. The packed column was surrounded by an air jacket, electrically heated to 78°±5° C. Constant temperature was maintained throughout the column at normal flow rates (0.2 to 2 ml./min.) by the ethanol preheater attached to the eluant intake tube, provided the length of the reflux tube was not less than 25 cm. When used with the 2.8 cm. diameter apparatus, the size of the preheater and the current passing through it were both increased to maintain the temperature at the higher flow rate (5 ml./min.). Normally the elements were separated at 1.0 ml./min. when the smaller columns were employed, though a rate of 0.5 ml./min. was used with 6 *M* hydrochloric acid owing to the lower temperature (60° C.) required to prevent gas evolution.

A. The Separation of Milligram Amounts of the Alkaline Earths

Samples containing less than 40 mg. of each of the alkaline earths to be separated were dissolved in a minimum volume of the eluting agent to be used, at pH 2–4. Calcium–magnesium and calcium–strontium separations were attempted first, using 0.75 *M*, 1.0 *M*, and 1.5 *M* ammonium lactate at pH 7. The somewhat erratic results obtained initially were traced to the practice of degassing solutions before use by boiling, causing increases in the lactate concentration of as much as 25%. More efficient removal of dissolved air was obtained by degassing for 2 minutes, cold, with a filter pump, and the elution volumes became reproducible.

Trial runs were made to determine the position of the peak and the width of the elution band for each element, using precipitation and tracer techniques for identification. Subsequently, the separation was extended to include all six elements, eluting beryllium with 0.55 *M* lactate at pH 5, and the remainder with 1.5 *M* lactate at pH 7, though occasionally the radium was stripped off with 6 *M* hydrochloric acid. The percentage recovery of radium was determined from the α-disintegration rates before and after separation. Other elements were recovered as beryllium oxide, magnesium ammonium phosphate, calcium carbonate, strontium sulphate, and barium sulphate, using standard procedures (7).

Comparative separations of most of the foregoing elements were made using ammonium lactate, ammonium citrate, and also hydrochloric acid, as eluting agents. Similar attempts with versene and the ammonium citrate–versene mixtures used by Farabee (4) had to be discontinued, as no method of satisfactorily operating a column with these eluants at elevated temperatures and flow rates of approximately 1 ml./min. could be found.

B. The Separation of the Alkaline Earths Present in Milk Ash Samples

Preliminary experiments were done with 2.5 g. samples of milk ash (containing 16% calcium, 2% magnesium, and 35% phosphate), dissolved in 6 *M* hydrochloric acid. Strontium carrier (20 mg.) was added to the solution before it was evaporated just to dryness. The residue from this evaporation was taken up in a minimum of 1.5 *M* lactic acid, pumped free of air, and run onto the column at the rate of 1 ml./min.

During subsequent elution with 1.5 *M* ammonium lactate, ammonium oxalate was added to the eluate fractions to identify the calcium band, and at the first sign of a marked decrease in the calcium oxalate precipitate the next 50 ml. were collected as the strontium fraction. Following this, the barium and radium were stripped off together with 6 *M* hydrochloric acid. After the 50 ml. strontium fraction had been evaporated to 10–15 ml. the strontium was recovered as the sulphate, and any calcium carried with it removed by metathesis to the carbonate followed by a fuming nitric acid precipitation of strontium nitrate.

Following these tests both the sample and column size (but not the amount of strontium carrier added) were increased in order to obtain a measurable amount of fallout Sr^{90} activity in the separated strontium. In addition, recoveries were simplified by eluting the strontium with 6 *M* hydrochloric acid following the ammonium lactate separation of calcium.

RESULTS

A. The Separation of Milligram Amounts of the Alkaline Earths

(i) Ammonium Lactate Eluant

Preliminary measurements showed that calcium and magnesium were easily separable using ammonium lactate, and so this pair was chosen for a series of tests of the effects of concentration changes on the separation factor. In Fig. 1 the equilibrium distribution for each element (volume of eluate to the peak less the interstitial volume/weight of resin in grams) is plotted as a function of the ammonium lactate concentration. As shown in this figure, at three different molarities the ratio of Ca to Mg distribution coefficients remained essentially constant, despite the rapid change in equilibrium distributions at the higher molarities.

An upper limit to the molarity of the eluant is set by the requirement that the eluate volume to the first peak must be greater than the resin interstitial volume in order to prevent overlapping of adjacent bands. In the case of magnesium the ammonium lactate upper limit is 1.5 *M*. The separation of five elements at this concentration is shown in some detail in Fig. 3. The apparent improvement in ratios of distribution coefficients over those indicated by Lerner and Rieman (10) (see Table I) is attributed to the use of a higher elution temperature. Fig. 2 shows a typical elution curve for beryllium and magnesium. Here the limits of the lactate concentration for a complete, rapid separation are 0.55 *M* and 0.75 *M*. The unexpected broadness of the magnesium band in both

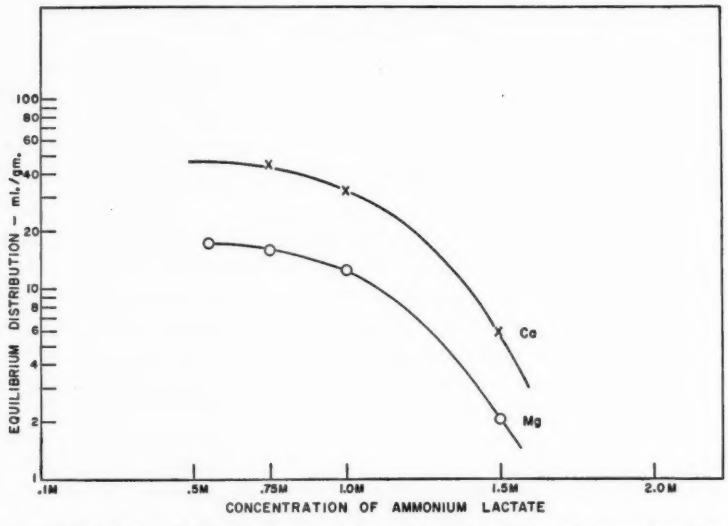

FIG. 1. The variation of distribution coefficient with concentration of ammonium lactate.

TABLE I

EFFECT OF ELUTING AGENT ON DISTRIBUTION COEFFICIENTS

Eluting agent	Ratios of distribution coefficients				
	Mg/Be	Ca/Mg	Sr/Ca	Ba/Sr	Ra/Ba
0.55 *M* amm. lactate pH 5	3.7				
0.75 *M* amm. lactate pH 7		2.8			
1.0 *M* amm. lactate pH 7		2.7			
1.2 *M* amm. lactate pH 7			1.5*	2.5*	
1.5 *M* amm. lactate pH 7		2.8	3.1	3.2	2.1
1.07 *M* HCl		~3†			
1.5 *M* HCl	2.3	4.0	<2.0	>3.0	
2.0 *M* HCl			1.8		
2.5 *M* HCl		3.3			
4.0 *M* HCl			2.3	3.0	
6.0 *M* HCl					1.1
5% amm. citrate pH 5.4		1.7	1.8	3.4	

Calculated from the data of Lerner and Rieman (10).
†*Calculated from the data of Campbell and Kenner (2).*

these figures is a result of the relatively large quantity of that element present in these samples (milliequivalents of magnesium = 8 × milliequivalents of strontium).

Yields measured under the conditions specified in Figs. 2 and 3 have been tabulated in Table II. It is apparent that quantitative separation of all six elements is possible within 5 hours, with one change of eluant required during that time. If preferred, the radium can be stripped off the column with 6 *M* hydrochloric acid immediately following the barium elution. The difference in the strontium recovery for samples containing 100 mg. of calcium (99.5%) and 400 mg. of calcium (88%) indicates the extent of column loading permissible in quantitative separations of this kind. These weights correspond

TABLE II

A SUMMARY OF QUANTITATIVE DATA OBTAINED WITH A VARIETY OF ELUTING AGENTS

	Yields*											
	Be		Mg		Ca		Sr		Ba		Ra (c.p.h.)	
Eluting agent	Added	Found	Added	Found	Added	Found	Added	Found	Added	Found	Added	Found
0.55 *M* amm. lactate pH 5	8.4	7.8†	38.2	38.7								
	10.5	10.6	39.4	39.2								
1.5 *M* amm. lactate pH 7					10.89	10.80	10.00	10.02	9.90	9.80		
			38.2	37.9	22.5	22.5	20.0	19.9	19.8	19.5		
			38.2	37.7	22.5	22.3	20.0	20.1	19.7	19.6	658	630
					100	Not measured	19.28	19.11				
					400	Not measured	20.0	17.6				
As above, followed by 6 *N* HCl									4.9	4.7	140	132
1.5 *M* HCl			39.4	39.2	22.5	22.5						
			8.36	8.15	26.2	26.3						
			8.36	8.39	27.0	26.8						
4.0 *M* HCl							19.4	19.5	20.0	20.0		
							10.2	10.1	9.97	9.91		

**All weights given in milligrams.*
†Low beryllium yield due to incomplete precipitation of hydroxide.

to a calcium uptake of 1.3 and 5 milliequivalents/g. of resin respectively, hence the column was completely in the calcium form in the second instance.

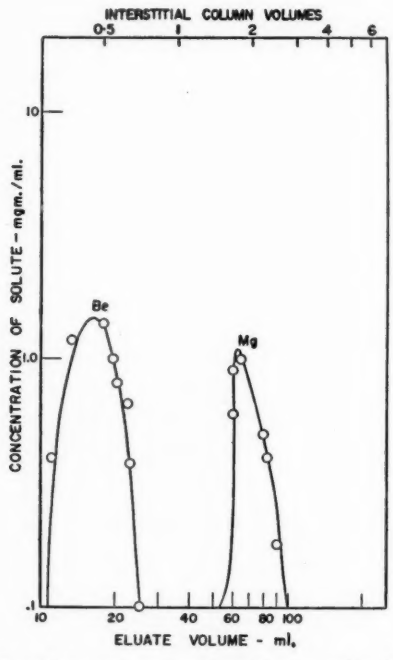

FIG. 2. The separation of beryllium and magnesium with ammonium lactate eluant—0.55 *M* at pH 5. 1.1×8 cm. column, flow rate 1.0 ml./min., $T = 78°$ C. (In this and all succeeding figures one interstitial volume has been subtracted from the eluate volume before plotting.)

(*ii*) *Hydrochloric Acid Eluant*

Fig. 4 shows a separation of beryllium, magnesium, calcium, strontium, and barium using 1.5 *M* hydrochloric acid as eluant, and Fig. 5 a separation of calcium, strontium, and barium using 4 *M* acid. The Mg/Ca and Ba/Sr ratios of distribution coefficients are slightly better than those for ammonium lactate, and the elements are more easily recovered quantitatively from the hydrochloric acid solutions. Diamond's (3) plot of distribution coefficient versus hydrochloric acid molarity indicates that the calcium–strontium separation should improve with increasing strength of the acid, to a maximum at 6 *M*. Despite the Sr/Ca distribution coefficient ratio increase from 1.8 in 2 *M* to 2.3 in 4 *M* acid, however, some overlapping of the fractions still occurs. This overlap and a similar one in the beryllium–magnesium separation in 1.5 *M* acid are partially the result of too fast flow rates (~1 ml./min.) for the lowered elution temperatures (60° C.), plus inadequate temperature control in these two cases, causing broadening of the elution bands. By reducing the column load, maintaining the temperature at 60° and the flow rate at 0.5 ml./min., the overlapping has been decreased, but the bands are still appreciably broader than those obtained with ammonium lactate or ammonium citrate eluant.

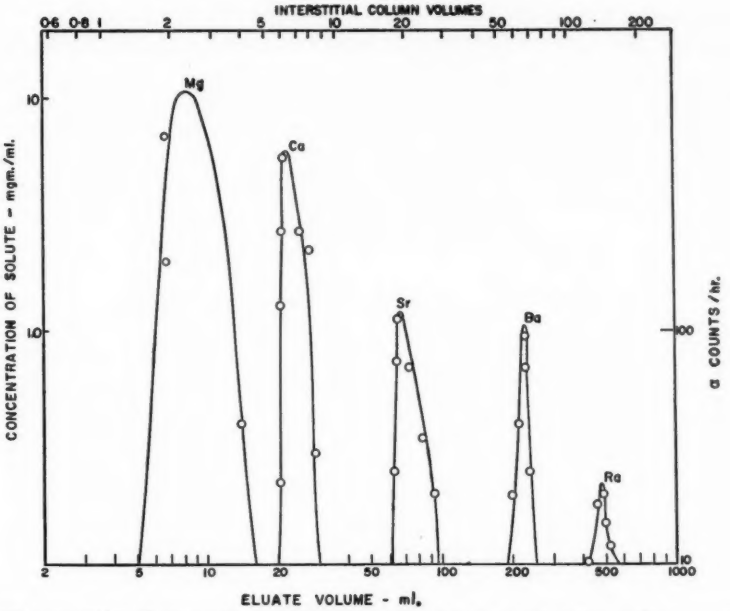

FIG. 3. The separation of magnesium, calcium, strontium, barium, and radium with ammonium lactate eluant—1.5 *M* at pH 7. 1.1×8 cm. column, flow rate 1.0 ml./min., $T = 78°$ C.

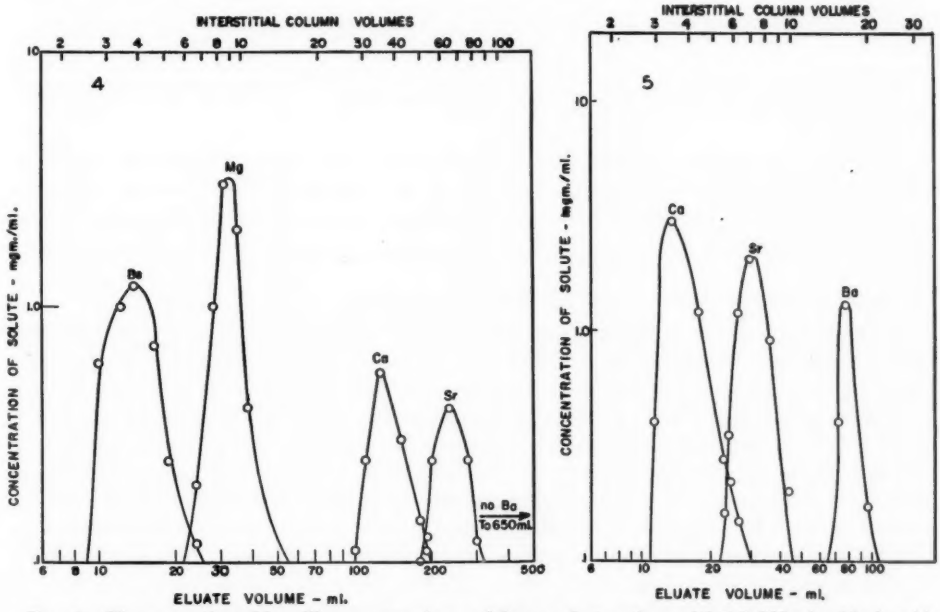

FIG. 4. The separation of beryllium, magnesium, calcium, and strontium with 1.5 *M* hydrochloric acid eluant. 1.1×8 cm. column, flow rate ~1.0 ml./min., $T \sim 60°$ C.

FIG. 5. The separation of calcium, strontium, and barium with 4 *M* hydrochloric acid eluant. 1.1×8 cm column, flow rate ~1.0 ml./min., $T \sim 60°$ C.

(iii) Ammonium Citrate Eluant

In order to achieve as rapid a separation of magnesium, calcium, strontium, and barium using ammonium citrate as with 1.5 *M* ammonium lactate, it was necessary to use a 5% citrate solution at pH 5. At that concentration the strontium–barium separation was the best obtained with any of the eluants, but it can be seen from Fig. 6 that some

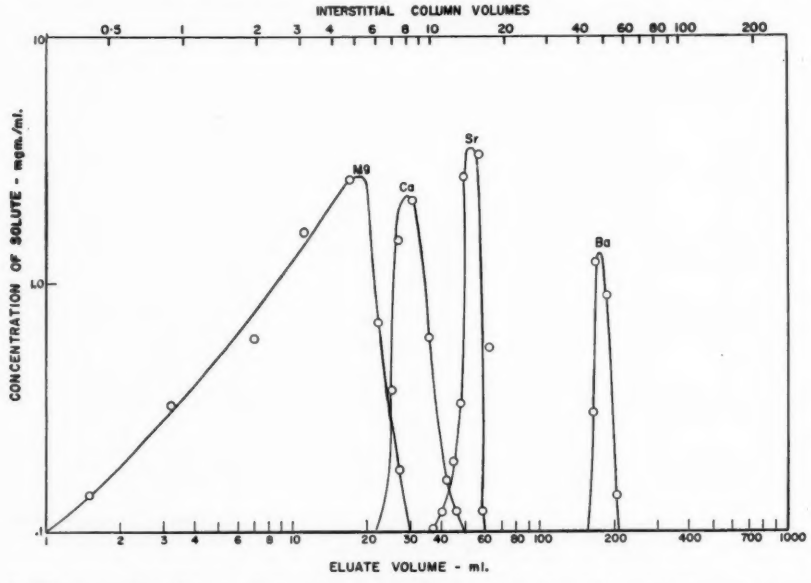

FIG. 6. The separation of magnesium, calcium, strontium, and barium with ammonium citrate eluant—5% at pH 5. 1.1×8 cm. column, flow rate 1.0 ml./min., $T = 78°$ C.

overlapping is present in the calcium–magnesium and strontium–calcium fractions. However, the ratios of distribution coefficients are sufficiently high that the suggested methods for the development of a quantitative hydrochloric acid separation are equally applicable to the use of this eluant.

B. Calcium–Strontium Separations in Milk Ash Samples

In order to analyze milk and bone ash samples for strontium, barium, and radium, which are present in amounts of <0.025% of the calcium, it is necessary to use an eluant effecting as large a separation of these elements from calcium as possible. As a result of the foregoing comparative study ammonium lactate was chosen as the most promising.

Fig. 7 shows the separation achieved with a 2.5 g. sample of ash on the small column. Phosphate is not held by the resin at all, appearing after the first column volume of eluate. At this extent of overloading both the magnesium and calcium appear in the eluate before all the sample is on the resin. This effect can be reduced somewhat by dilution of the sample solution, but since the end point of the calcium fraction and the beginning of the strontium appear to be unaffected by the overloading, the dilution seems unnecessary. The strontium yield for this separation was 88%, and the calcium present in this strontium fraction was less than 0.05 mg.

From these data for a column loaded to capacity (5 milliequivalents of calcium/g. of resin), it became obvious that approximately seven times the weight of resin in this column would be required to separate satisfactorily 20 mg. of strontium from a 15–17 g. sample of ash. Fig. 8 shows a typical elution curve of a 15 g. sample from the larger column. The strontium yield of 84% from the 300–650 ml. fraction contained 0.24 mg. of calcium. Another 6% of the strontium was recovered from the last 20 ml. of the calcium fraction, containing 1.5 mg. of calcium. Since the increase in volume of eluate

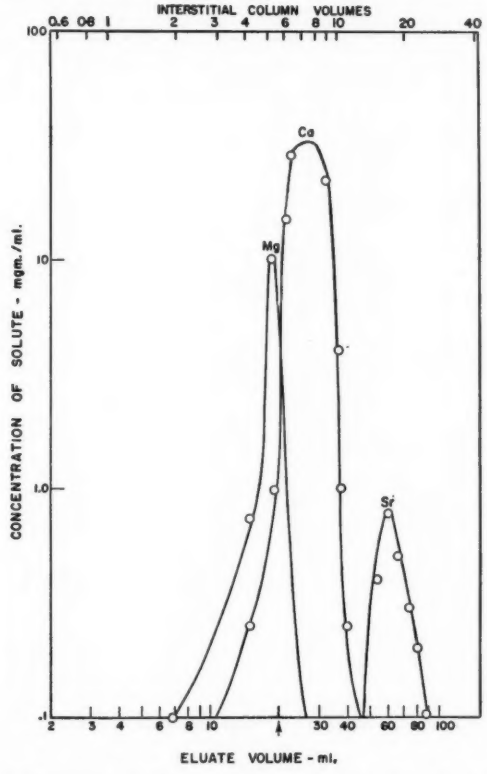

FIG. 7. The separation of magnesium, calcium, and strontium from 2.5 g. of milk ash, with ammonium lactate eluant—1.5 *M* at pH 7. 1.1×8 cm. column, flow rate 1.0 ml./min., $T = 78°$ C. (The arrow indicates the volume of the sample solution.)

to the strontium peak in Fig. 8 over that in Fig. 3 (70 ml. to 350 ml.) can be accounted for by the increase in area of column (factor of 5), it may be inferred that the decrease in strontium yield was a result of the broadening of the calcium peak until an appreciable overlap of the two fractions existed. However, by a further increase in the amount of resin used, this overlap has been eliminated, and over 35 routine analyses have now been made with this column, with strontium recoveries varying between 85 and 95%.

The method has also been applied to the determination of much smaller quantities of strontium in bulk amounts of milk ash. Traces of strontium ranging from 0.6 to 2 mg. have been separated from samples containing approximately 2.5 g. of calcium and

0.3 g. of magnesium, and the total strontium present in these samples (70–130 p.p.m.) calculated by utilizing the percentage recovery of known amounts of strontium activity (see Table III). The reliability of the method when used in such determinations is demonstrated by the nearly quantitative recovery of added activity in sample 2 (*a*), while in the other samples the yield was deliberately lowered by repeated chemical purifications to ensure the constant specific activity of the strontium precipitate.

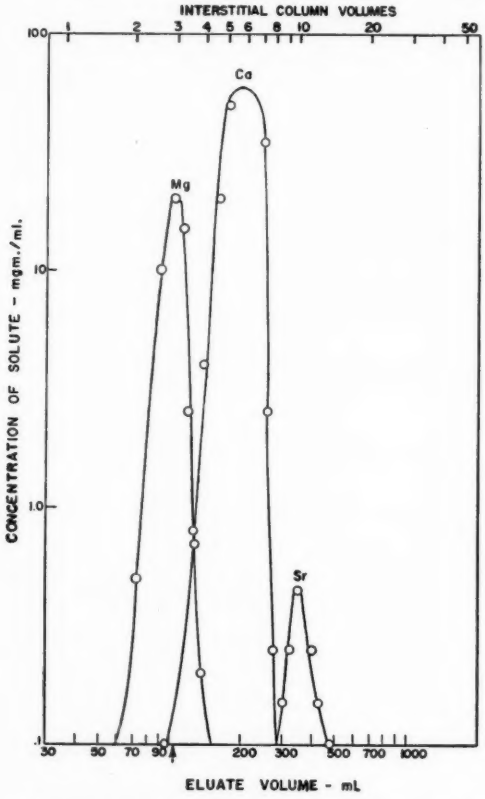

FIG. 8. The separation of magnesium, calcium, and strontium from 15 g. of milk ash, with ammonium lactate eluant—1.5 *M* at pH 7. 2.8×9 cm. column, flow rate 5.0 ml./min., T = 78° C. (The arrow indicate the volume of the sample solution.)

TABLE III

DETERMINATION OF NATURALLY OCCURRING STRONTIUM IN MILK

Sample	Weight (g.)	Strontium activity added (dis./min.)	Strontium activity recovered (dis./min.)	Weight strontium recovered (mg.)	Total strontium in sample (mg.)	p.p.m. strontium in sample	Ca/Sr in sample
1	15	24	13.5	0.6	1.07	71	2240
2 (*a*)	17	198	180	1.99	2.2	130	1140
2 (*b*)	17	198	105	1.03*	2.0	120	1250

**Sample 2 (b) is the result of subjecting sample 2 (a) to repeated chemical separations to test the purity of the strontium carbonate precipitate, and hence the yield is very low.*

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THE POLYMERIZATION OF METHACRYLONITRILE AT ELEVATED TEMPERATURES[1]

S. BYWATER

ABSTRACT

The photosensitized polymerization of methacrylonitrile has been investigated at temperatures above 100° C. A study of the kinetics suggests that at these temperatures the reverse (depropagation) reaction is important. From the experimental data, the heat and entropy change for the polymerization has been calculated.

INTRODUCTION

Dainton and Ivin (5) have indicated the reversible nature of polymerization and shown how heats and entropies of polymerization may be obtained from 'ceiling temperature' phenomena. Heats and entropies of polymerization may be obtained in this way for methyl methacrylate (2, 7, 10). Further information on other monomers would be of interest in order to obtain more data on heats and entropies of polymerization. It is desirable to choose a monomer where the reverse reaction yields predominantly monomer rather than larger fragments. Kern and Fernow (8) have reported an 85% yield of monomer in the depolymerization of polymethacrylonitrile so this compound is suitable for a study of reversible polymerization.

EXPERIMENTAL

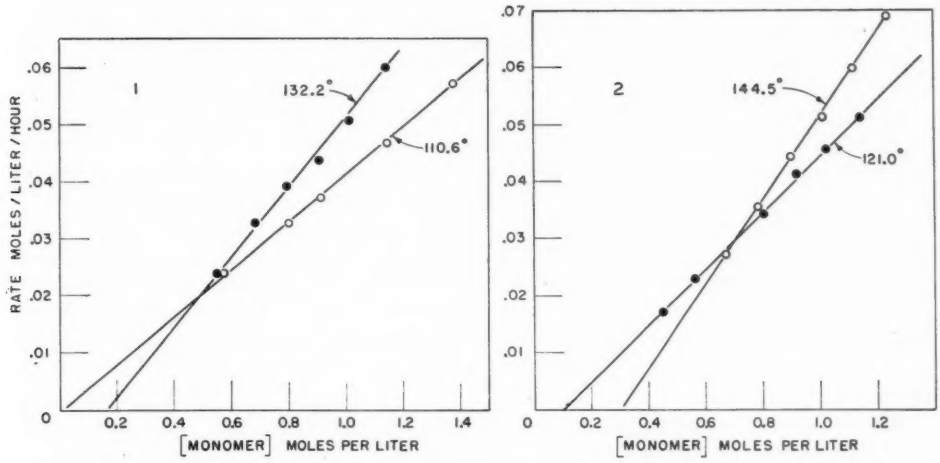
The apparatus used was identical with that described previously (2). *o*-Dichlorbenzene was not used as solvent in this case since, although it is an efficient photosensitizer for methacrylonitrile, the polymer precipitates. Benzonitrile was found to be suitable for use as solvent since the polymer is soluble in this solvent. It does not, however, function as a photosensitizer and it was necessary to add one which is thermally stable to 150° C. Benzoin appears to fulfill these requirements (10) and was used throughout these experiments at a concentration of 0.0089 molar. Light from the mercury arc was filtered through an 0-52 Corning filter in order to remove the shorter wavelength radiation where benzoin has a strong absorption (3). C. P. benzoin was recrystallized twice from benzene before use. Methacrylonitrile was supplied by the Shell Development Co. and distilled under nitrogen before use. Benzonitrile (Eastman Kodak white label) was distilled prior to use. Methacrylonitrile was estimated in 1 ml. samples by the mercaptan addition method of Beesing *et al.* (1); since, however, mercaptans add to methacrylonitrile more slowly than to acrylonitrile, the analysis solutions were left standing 40 minutes in a thermostat bath at 35° before titration. Blank experiments showed that methacrylonitrile could be analyzed successfully by this method.

RESULTS

The rate of polymerization was studied at four temperatures, 110.6°, 121.0°, 132.2°, and 144.5°, as a function of monomer concentration. Methacrylonitrile shows very slow rates of polymerization (4) compared to other monomers so it was not possible to show

[1]*Manuscript received January 25, 1957.*
Contribution from the Division of Applied Chemistry, National Research Council, Ottawa, Canada.
Issued as N.R.C. No. 4321.

that at high conversions the monomer concentration tends to an equilibrium value as was done previously for methyl methacrylate. Rates of monomer disappearance were studied up to 15% conversion, the plots being slightly curved. Initial rates were plotted as a function of monomer concentration and are shown in Figs. 1 and 2. The figures show that initial rates of polymerization are first order with respect to monomer concentration



FIGS. 1 and 2. Initial rates of polymerization as a function of initial monomer concentration at four temperatures.

but as the temperature increases, an increasing intercept is found on the x-axis corresponding to a monomer concentration at which the polymerization rate falls to zero. The slopes of the lines were plotted against reciprocal temperature in Fig. 3 giving an activation energy of 5.4 kcal.

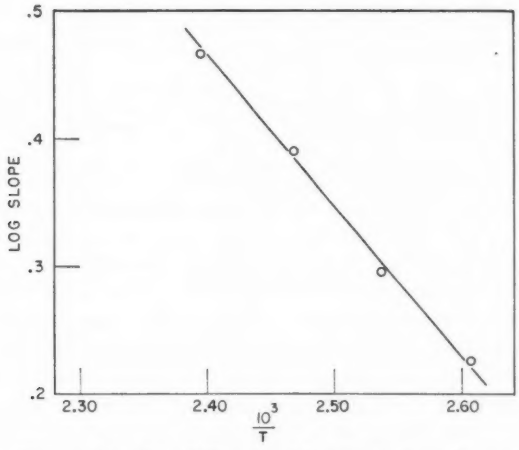


FIG. 3. Slopes of the plots of Figs. 1 and 2 versus reciprocal temperature.

DISCUSSION

The scheme of polymerization given by the present author (2) substituting benzoin for the solvent as photosensitizer should hold for the present polymerization. This yields the rate expression

$$-d(M)/dt = k_p f(I_0)^{\frac{1}{2}} k_t^{-\frac{1}{2}} \{[M]_0 - [M]_e\}$$

in the non-integrated form since we are dealing with initial rates only. Here $[M]_0$ is the initial monomer concentration, $[M]_e$ an equilibrium monomer concentration, k_p and k_t the rate constants for chain propagation and termination respectively, and $f(I_0)$ some function of the incident light intensity and the benzoin concentration. This relation requires that at each temperature the initial rates should be first order in monomer concentration but the rate should fall to zero as the monomer concentration is reduced to the equilibrium value $[M]_e$, which is the critical concentration at which the velocity of chain propagation becomes equal to that of depropagation or 'unzipping' of the chain. The experimental data conform to this equation, enabling $[M]_e$ values to be obtained. The slopes of the first order plots should be a function of $k_p\, k_t^{-\frac{1}{2}}$ according to the above equation, and making the reasonable assumption that $f(I_0)^{\frac{1}{2}}$ is temperature independent the activation energy from Fig. 3 should correspond to $E_p - \frac{1}{2}E_t = 5.4$ kcal. Grassie and Vance (6) obtained a value of 6.5 kcal. for this ratio at lower temperatures where depropagation is negligible.

The equilibrium monomer concentration is related to the standard Gibbs free energy of polymerization by the relation (2)

$$-\Delta G_{ss}/RT = \ln(1/[M]_e)$$

where ΔG_{ss} is the Gibbs free energy change in the polymerization at a standard state of 1 mole per liter.

Thus $\Delta G_{ss}/RT$ can be computed from the intercepts of the lines in Figs. 1 and 2 (Table I). $\Delta G_{ss}/RT$ is plotted against $10^3/T$ in Fig. 4. The slope of this line (corresponding to ΔH_{ss}) is equivalent to -15.3 kcal. Substitution of this value into ΔG_{ss} gives $\Delta S_{ss} = -34$ e.u. It is estimated that the uncertainty in these determinations amounts to ± 1 kcal. in ΔH and ± 2 e.u. in ΔS. No direct calorimetric data on the heat of polymerization of methacrylonitrile exist but Tong and Kenyon (12) report a heat of polymerization of acrylonitrile (liquid monomer–solid polymer) of -17.3 kcal. α-Methyl substitution lowers the heat of polymerization by several kilocalories; thus the heat of polymerization of the most closely similar monomer, acrylic acid, is lowered by 2.8 kcal. on α-methyl substitution. Thus the present value for the heat of polymerization appears reasonable. The entropy of polymerization is slightly larger than that reported for methyl methacrylate (2) ($\Delta S_{ss} = -29.5$ e.u.) but not greatly different. Calculations of ΔH_{1c} and ΔS_{1c} (2) have not been carried out since benzonitrile is not reported (9) to be a 'good' solvent for

TABLE I

T (° K.)	$[M]_e$ (moles/liter)	$-\Delta G_{ss}/RT$
394.2	0.09	2.40
405.4	0.15_5	1.87
417.7	0.27	1.31

polymethacrylonitrile and hence the μ value characterizing polymer–solvent interaction required for the correction term is not easily estimated. This can be done should more data become available on the thermodynamics of solutions of this polymer.

There undoubtedly exist side reactions in this type of polymerization. Talât-Erben and Bywater (11) have indicated abnormal steps in the propagation steps and the fact that the yield of monomer in degradation is not 100% (8) suggests that side reactions

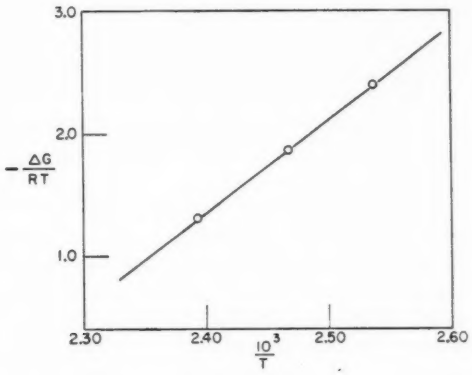


FIG. 4. $\Delta G_{ss}/RT$ as a function of reciprocal temperature.

also may occur in the depropagation steps. The kinetics however clearly indicate that both chain propagation and the reverse (depropagation) steps occur in methacrylonitrile above 110° C. and it seems doubtful whether the effect on the measured ΔH and ΔS values for the process could be much larger than the estimated error in their determination.

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CONSTITUTION OF A WATER SOLUBLE HEMICELLULOSE FROM AMERICAN BEECHWOOD (FAGUS GRANDIFOLIA)[1]

G. A. ADAMS

ABSTRACT

Extraction of beechwood chlorite holocellulose with hot water yielded a hemicellulose in 13.4% yield (based on original extractive-free wood) containing D-xylose 72%, D-galactose 11.0%, and uronic acid 13.2%. Purification of the crude hemicellulose by complexing with Fehling's solution yielded a chemically homogeneous fraction containing D-xylose 83% and 4-*O*-methyl-D-glucuronic acid 15.5%. Hydrolysis of the fully methylated hemicellulose yielded 2,3,4-tri-*O*-methyl-D-xylose, 2,3-di-*O*-methyl-D-xylose, 3-*O*-methyl-D-xylose, and 3-*O*-methyl-2-*O*-(2,3,4-tri-*O*-methyl-D-glucopyranosyluronic acid)-D-xylose in a molar ratio of 2:35:3:5. On the basis of the methylation data, periodate oxidation, reducing power determinations, and weight average molecular weight values a possible structure for the hemicellulose is proposed.

Existence of a xylan in beechwood was established by Wheeler and Tollens in 1889 (16) by identification of *D*-xylose in an acid hydrolyzate of beechwood sawdust. Later O'Dwyer (12) isolated hemicelluloses A and B from beechwood by extraction with sodium hydroxide and showed them to differ in physical and chemical properties. A recent investigation of the structure of hemicellulose A (3) showed it to be a straight chain of about 70 1 → 4 linked β-D-xylopyranose residues to which a terminal 4-*O*-methyl-D-glucopyruronic acid residue is linked through $C_{(2)}$ to every 10th xylose unit. On the basis of fractionation experiments with hemicellulose A acetates, O'Dwyer (13) has suggested that this material may contain as many as three separate hemicelluloses; this suggestion is not improbable considering the complexities usually found in most polysaccharides of plant origin. The present study was undertaken to investigate the possibility of preparing a hemicellulose from beechwood by the use of a milder solvent than 4% sodium hydroxide. The constitution of a hemicellulose extracted by water forms the main subject of the investigation.

The starting material was holocellulose prepared by chlorite delignification of American beechwood (*Fagus grandifolia*). Although Timell and Jahn (15) have shown that the polysaccharides of birch undergo degradation during this treatment, there is also evidence that the degradation is neither extensive (17) nor selective (7). Extraction with heated water (94° C.) produced an extracting medium which was slightly acid (pH 5.1) and hence may have had a degrading effect on the hemicelluloses, thereby increasing their solubility in water. That such an effect was minimal was demonstrated by the fact that there was no change in the viscosity of the isolated hemicellulose after it was heated for 24 hours in aqueous solution (final pH 5.1). Chromatographic examination of the heated solution showed no evidence of cleavage products. Hence it may be concluded that the water extraction removed a pre-existent hemicellulose component from the holocellulose.

The isolated hemicellulose (13.4% yield) contained xylose and a monomethyl uronic acid as the major constituents; a small amount of galactose was also present. Purification by complexing with Fehling's solution removed the galactose and yielded a hemicellulose containing D-xylose 83%, uronic acid 15.5%, and having $[\alpha]_D^{25} -75°$ (in water).

The uronic acid was separated from the neutral sugars after hydrolysis as an aldobiouronic acid. Its constituents were determined by reducing its methyl ester methyl

[1]*Manuscript received January 24, 1957.*
Contribution from the Division of Applied Biology, National Research Laboratories, Ottawa.
Issued as N.R.C. No. 4326.

glycoside with lithium aluminum hydride to the corresponding disaccharide, methyl-*O*-(4-*O*-methyl-D-glucopyranosyl)-D-xyloside. Acid hydrolysis yielded D-xylose and 4-*O*-methyl-D-glucose and hence the acid constituent was identified as 4-*O*-methyl-D-glucuronic acid. The high positive rotation of the aldobiouronic acid (+79°) indicated an α-configuration for the glycosidic bond.

The hemicellulose was methylated and fractionally precipitated from chloroform solution by petroleum ether to give one main fraction having theoretical methoxyl content. Methanolysis and hydrolysis yielded the following products: (I) methylated uronic acid, (II) 3-*O*-methyl-D-xylose, (III) 2,3-di-*O*-methyl-D-xylose, and (IV) 2,3,4-tri-*O*-methyl-D-xylose; the molar ratio of these fractions was approximately 5:3:35:2.

The linkage between the D-xylose residue and the 4-*O*-methyl-D-glucuronic acid was established by examination of the methylated aldobiouronic acid Fraction I. Reduction of its methyl ester methyl glycoside with lithium aluminum hydride followed by hydrolysis of the disaccharide yielded 3-*O*-methyl-D-xylose and 2,3,4-tri-*O*-methyl-D-glucose. These results showed that the uronic acid was glycosidically attached to the D-xylose unit through $C_{(2)}$ or $C_{(4)}$. The exact point of attachment was established by reducing the original aldobiouronic acid with lithium aluminum hydride to the corresponding disaccharide, 4-*O*-methyl-D-glucosyl-D-xylose. The disaccharide was then fully methylated and on hydrolysis yielded 3,4-di-*O*-methyl-D-xylose and 2,3,4,6-tetra-*O*-methyl-D-glucose. These results proved that the attachment of the uronic acid moiety was to $C_{(2)}$ of the xylose unit. Therefore the aldobiouronic acid derived from the hemicellulose by acid hydrolysis was 2-*O*-(4-*O*-methyl-α-D-glucopyranosyl uronic acid)-D-xylopyranose.

The 2,3,4,-tri-*O*-methyl-D-xylose represented the terminal xylopyranose units in the original methylated hemicellulose and the amount indicated that there was one non-reducing end group present for every 25 sugar residues. The relatively large proportion of 2,3-di-*O*-methyl-D-xylose proved that the main chain of the hemicellulose was composed of xylopyranose units linked through $C_{(1)}$ and $C_{(4)}$. The change in rotation of the methylated polysaccharide on hydrolysis from negative (−102°) to positive (26°) indicated that the xylose units were mainly in the β-configuration. The 3-*O*-methyl-D-xylose in the hydrolyzate from the methylated hemicellulose indicated branch points in the molecule. The amount of 3-*O*-methyl-D-xylose exceeded the amount of 2,3,4-tri-*O*-methyl-D-xylose originating from the non-reducing end groups and it must be concluded that not all of the monomethyl pentose was structurally significant. It was considered likely that incomplete methylation and demethylation on hydrolysis contributed partly to the production of the monomethyl sugar. Its possible origin from cleavage of the methylated aldobiouronic acid was discounted, as no free methylated glucuronic acid was found in the hydrolyzate from the methylated hemicellulose.

On the basis of the methylation data it is possible to propose a structure for the hemicellulose consisting of 45 D-xylopyranose units linked $1 \rightarrow 4$ by β-glycosidic bonds. The xylan chain contains one branch point at $C_{(2)}$ of a xylose unit and hence the molecule has two non-reducing end groups and one reducing end group. Five units of 4-*O*-methyl-D-glucuronic acid are joined as single terminal side chains to the xylose units of the main structure by α, $1 \rightarrow 2$ glycosidic bonds. The distribution of the uronic acids units along the xylan chain is unknown except that they cannot be attached to the units forming the branch point or the non-reducing end. Periodate oxidation data provided confirmation of the structure as proposed from the methylation data. The proposed structure should consume 1.08 moles of periodate and produce 0.08 moles of formic acid

per mole of anhydropentose unit; actual consumption of periodate was 0.98 moles and formic acid production was 0.09 moles per sugar unit. On the basis of formic acid production (assuming two non-reducing ends) the molecule would contain 44 sugar units. The foregoing evidence was supported further by an estimate of reducing power, which indicated one reducing group per 47–51 sugar residues. Viscosity measurements of the hemicellulose, which yield weight average molecular weight values, were made in 0.1 *M* sodium chloride and in cupriethylenediamine and gave values of 46 and 47 respectively. Although the viscosity data as calculated from Staudinger's equation may be slightly anomalous owing to a branched molecule, the presence of one branch point is not likely sufficient to affect the general order of the result.

This hemicellulose isolated from American beechwood by aqueous extraction differed in some respects from the European beechwood studied by Aspinall *et al.* (3). While the constituents are the same, the American beechwood hemicellulose was a smaller molecule and was singly branched. The hemicellulose of the European beechwood was prepared by alkaline extraction of the wood (11) and may have included a water soluble hemicellulose similar to that isolated from American beechwood. The presence of branched material in the hemicellulose studied by Aspinall *et al.* (3) might have accounted in part for the presence of the monomethyl xylose formed on methanolysis of the methylated hemicellulose. A singly branched xylan containing a terminal D-glucuronic acid residue has been isolated from pear cell wall (5), but unlike the beechwood xylan, had the uronic acid attached to $C_{(3)}$ of the xylose unit. As pointed out previously (1) the presence of a methyl ether substituent on $C_{(4)}$ of D-glucuronic acid is associated with glycosidic linkage attachment to $C_{(2)}$ of the xylose residue. However, a recent investigation (4) of Monterey pine (*Pinus radiata*) has shown the presence of a small amount of 3-*O*-α-(4-*O*-methyl-D-glucuronosyl)-D-xylose along with the usual 2-*O*-(4-*O*-methyl-D-glucuronosyl)-D-xylose, and the authors have predicted that the former acid may be a fairly common acidic constituent of wood hemicelluloses.

EXPERIMENTAL

All specific rotations are equilibrium values unless otherwise stated and melting points are corrected.

Paper Chromatography

The following solvents (v/v) were used to separate the sugars and their derivatives: (A) ethyl acetate:pyridine:water (2:1:2), (B) methyl ethyl ketone:water (2:1), (C) ethanol:benzene:water (47:200:15), (D) *n*-butanol:ethanol:water (40:11:19), and (E) ethyl acetate:acetic acid:formic acid:water (18:3:1:4). Separations were performed by the descending technique on Whatman No. 1 filter paper. A 3% solution of *p*-anisidine in ethanol was used as the spray reagent. The R_g values are mobilities relative to 2,3,4,6-tetra-*O*-methyl-D-glucose.

Preparation of Hemicellulose

Shavings were prepared from a mature American beechwood log (*Fagus grandifolia*) and were ground in a Wiley mill. The fraction passing 20 mesh and retained on 60 mesh was successively extracted with benzene–ethanol (2:1) and ethanol. Pectic substances were removed by extraction with ammonium oxalate (0.5%) at 85° C. for two periods of 3 hours each; the residue was thoroughly washed with water at 85° C. Holocellulose was prepared from the extractive-free wood by the acid chlorite method (18) in 80.5%

yield. Holocellulose (600 g.) was suspended in 35 liters of water and stirred continuously for 24 hours at 94° C. The pH of the solution was initially 5.5 and decreased over the 24 hour period to 5.1. The extract was filtered through cloth, centrifuged to remove cellulosic fibers, and concentrated 10-fold at 25° C. in a Majonnier evaporator. The concentrated solution was poured into 4 volumes of ethanol and after it had been left overnight the precipitated hemicellulose was recovered by filtration. Drying with ethanol and ether yielded a fine white powder, yield 13.4% (based on extractive-free wood), ash 6.5%, moisture 8.4%. Determination of uronic acid (6) required substantially ash-free material and the ash content was reduced to <0.1% by the following procedure: hemicellulose (2 g.) was dissolved in 100 ml. of water to which were added *N* hydrochloric acid (10 ml.) and 95% ethanol (25 ml). The mixture was kept at 5° C. for 1.5 hours with frequent shaking. The hemicellulose was precipitated into 420 ml. of absolute ethanol and washed free of acid, after which it was taken up in water and freeze-dried. Analysis showed that the hemicellulose was composed of uronic acid 13.2%, xylose 72.0%, and galactose 11.0%.

Purification of the Water Soluble Hemicellulose

Hemicellulose (50 g.) was dissolved in 4% sodium hydroxide (3500 ml.) and mixed with Fehling's solution (3000 ml.). The copper complex which formed was filtered off, decomposed with hydrochloric acid in acetone (25:600 v/v), and the polysaccharide was washed free of acid with acetone:water (60:40 v/v) and dried *in vacuo*. Chromatographic examination of the product after acid hydrolysis showed that xylose was the only neutral sugar present. Anal.: xylose 83.8%, uronic acid 15.5%, ash 0.35%, $[\alpha]_D^{25} -75° \pm 2°$ (*c*, 1.0% in 1% sodium hydroxide).

Preparation of Uronic Acids from the Hemicellulose

Hemicellulose (100 g.) was stirred overnight in *N* sulphuric acid (2000 ml.) at room temperature; during this time the solution became dark brown. Heating at 98° C. for 7 hours hydrolyzed the polysaccharide to a constant reducing value. The solution was brought to pH 6.0 by the addition of barium hydroxide, filtered free of barium sulphate, and the cations were removed by passage through a column of Amberlite IR-120. The solution and washings were concentrated to about one-quarter of their volume at 30° C. The uronic acid components were absorbed on a column of Dowex 1-X[4] (HCO_3^-) (20×150 mm.). The column was washed with water until free of sugars by the anthrone test. Uronic acids were displaced from the resin by addition of excess 0.1 *N* sodium hydroxide and cations were removed from the solution by Amberlite IR-120. The acidic solution was concentrated to a sirup and freeze-dried, yield 11.34 g. Chromatographic examination in solvent E showed the presence of five components with R_x values (movement relative to xylose) as follows: 0.09, 0.27, 0.35, 0.70, and 1.30 (Fractions 1, 2, 3, 4, and 5); of these, Fraction No. 4 (R_x 0.70) was the largest component. Fraction No. 5 was chromatographically identical with 4-*O*-methyl-D-glucuronic acid.

The uronic acid fractions (6.7 g.) were separated chromatographically on sheets of Whatman No. 1 filter paper ($18\frac{1}{4} \times 11\frac{1}{4}$ in.) using solvent E. The acid fractions were eluted with water, concentrated at 30° C., and dried *in vacuo* to constant weight.

Examination of the Uronic Acid Fractions

Samples of Fractions 1, 2, 3, and 4 (approximately 20 mg. each) were hydrolyzed in sealed tubes with *N* sulphuric acid for 18 hours at 110° C. Considerable decomposition

occurred. Neutralization with barium carbonate and clarification with charcoal followed by chromatographic examination in solvents A and E showed xylose and 4-*O*-methyl-D-glucuronic acid to be the main components of all fractions; traces of glucose were also present. Fractions 1 and 2 contained a small amount of galacturonic acid which was thought to have its origin in a pectic contaminant. Since all fractions had essentially the same components, Fraction 4, being the largest, was chosen for further examination.

Uronic Acid Fraction 4

This material was an aldobiouronic acid, acid equivalent 347 (calculated for $C_{12}H_{19}O_{11}$, acid equivalent 340), $[\alpha]_D^{25}$ $+79°\pm2°$ (in water), R_x 0.66–68 (solvent E). Identification of the constituents of this acid was made as follows: the methyl ester methyl glycoside of the acid was prepared by refluxing the aldobiouronic acid in 2% methanolic hydrogen chloride for 8 hours. The product (354 mg.) was dissolved in dry tetrahydrofuran (20 ml.) and added dropwise to a suspension of lithium aluminum hydride (0.7 g.) in tetrahydrofuran (35 ml.) over a period of 1 hour. The reaction mixture was then refluxed gently for an additional hour, cooled, and excess lithium aluminum hydride was decomposed by addition of ethyl acetate and then water. The precipitated salts were filtered off and the solution was deionized by a mixture of Amberlite IR-120 and IR-4B. The recovered disaccharide weighed 284 mg. Hydrolysis with 0.5 *N* sulphuric acid for 8 hours at 100° C. yielded a sirup which on qualitative chromatographic examination using solvent C showed spots corresponding to D-xylose and 4-*O*-methyl-D-glucose. The sugars were separated chromatographically on large sheets of Whatman No. 1 paper using solvent C. Elution with water yielded D-xylose (91 mg.), m.p. and mixed m.p. 145° C., $[\alpha]_D^{25}$ $+18°\pm0.5°$ (*c*, 0.8% in water), and sirupy 4-*O*-methyl-D-glucose (111 mg.). Anal.: calculated for $C_7H_{14}O_6$: OCH_3 16.0%; found: OCH_3 15.4%.

The osazone of the 4-*O*-methyl-D-glucose was prepared by heating the sugar (90 mg.) with water (3.5 ml.), acetic acid (0.3 ml.), and phenylhydrazine (0.5 ml.) for 2.5 hours at 90° C. The recovered 4-*O*-methyl-D-glucosazone was recrystallized from ethanol containing a small amount of water and had a melting point of 157–158° C., unchanged on admixture with an authentic sample.

Methylation of Hemicellulose

Hemicellulose (15 g.) was methylated with dimethyl sulphate and sodium hydroxide by a method previously described (2). Two methylations were applied successively, after which the crude product was recovered by neutralization, dialysis, and evaporation. After a total of 10 methylations the product was soluble in methyl iodide and was subjected to four methylations by Purdie's reagents. The recovered product had a methoxyl content of 37.5%. Methylation with diazomethane increased the methoxyl content to 38.1%, a value which was not increased by further methylation. The infrared spectrum showed no hydroxyl band at 3500 $cm.^{-1}$. The fully methylated hemicellulose was a porous yellow solid, yield 13.6 g., OCH_3 38.1% (theoretical value for dimethyl xylan 38.7%), $[\alpha]_D^{25}$ $-102°\pm1°$ (*c*, 0.9% in chloroform).

Fractionation of Methylated Hemicellulose

The methylated hemicellulose (13.0 g.) was dissolved in chloroform solution, clarified by centrifuging, and fractionally precipitated by the addition of petroleum ether (b.p. 30°–60° C.). With the exception of small head and tail fractions, the main bulk

of the hemicellulose precipitated as one fraction, yield 12.5 g., OCH_3 38.2%, $[\alpha]_D^{25}$ $-102°\pm1°$ (*c*, 1.0% in chloroform).

Methanolysis

The fully methylated hemicellulose (50 mg.) was heated with 8% methanolic hydrogen chloride (5.0 ml.) in a boiling-water bath for 12 hours. Solvent was removed, 0.5 *N* hydrochloric acid (5 ml.) was added, and the methyl glycosides were hydrolyzed for 8 hours at 100° C. to yield a mixture of methylated sugars, $[\alpha]_D^{25}$ $+26°\pm1°$. The sugars were recovered and chromatographed in solvent B, using *p*-anisidine as the indicating spray. Authentic samples of 3-*O*-methyl-D-xylose, 2,3,-di-*O*-methyl-D-xylose, and 2,3,4-tri-*O*-methyl-D-xylose were used as reference compounds. A total of four spots appeared on the chromatogram and the following tentative identifications were made, based on mobility of the substances relative to the reference compounds: methylated uronic acid (I), a monomethyl pentose corresponding to 3-*O*-methyl-D-xylose (II), a dimethyl pentose corresponding to 2,3,di-*O*-methyl-D-xylose (III), and a trimethyl pentose corresponding to 2,3,4-tri-*O*-methyl-D-xylose (IV). The yield of Fraction I was determined by isolation as described later. Quantitative chromatography of the sugars on paper, elution with water, and analyses by the alkaline hypoiodite method (5) showed Fractions I, II, III, and IV to be present in a simple molar ratio of 5:3:35:2.

Separation of Methylated Sugars

The fully methylated hemicellulose (6.7 g.) was refluxed with methanolic hydrogen chloride (8%) for 10 hours, when the rotation became constant. After neutralization of acid with silver carbonate and recovery of glycosides and uronosides by the usual method, the latter were converted to their barium salts by heating at 65° C. for 2 hours with a saturated solution of barium hydroxide (80 ml.). Excess barium hydroxide was removed by carbon dioxide.

The fully methylated glycoside fraction was recovered by continuous extraction with *n*-pentane (yield 0.469 g.). The aqueous residue was freed of cations by Amberlite IR-120 and the uronic acid glycoside was absorbed on Amberlite IR-4B (acetate form). Thorough washing of the resin yielded the sugar glycosides (5.82 g.). The acid fraction was recovered by elution with 0.1 *N* formic acid, yield 0.84 g. Hydrolysis and chromatography showed that the trimethyl glycoside fraction contained some dimethyl glycosides and also that the uronic acid fraction contained some monomethyl glycoside. The various glycoside fractions were hydrolyzed to reducing sugars by 0.5 *N* hydrochloric acid and these were separated on Celite columns (10) using butanol saturated with water as solvent. Butanol saturated with 0.25% ammonium hydroxide was used when uronic acid was separated from sugars. The uronic acid fraction was recovered by eluting the column with water. A total of four separate fractions was recovered, which corresponded to Fractions I, II, III, and IV as found on the paper chromatograms previously described.

Examination of the Methylated Sugar Fractions

Fraction I.—This material was a methylated aldobiouronic acid which gave a cherry red spot with *p*-anisidine spray on a paper chromatogram, OCH_3 38.8%, acid equivalent 412 (calculated for $C_{16}H_{28}O_{11}$: OCH_3 39.2%, acid equivalent 396). Identification of the constituents of the aldobiouronic acid was made as follows: The aldobiouronic acid (422 mg.) was converted to its methyl glycoside methyl ester by refluxing for 6 hours with 8% methanolic hydrogen chloride (25 ml.). The acid was neutralized with silver

carbonate, silver salts were removed by filtration, and the solvent was removed by evaporation. The product was dissolved in dry ethyl ether (25 ml.) and the solution was added dropwise over a period of 1 hour to a stirred suspension of lithium aluminum hydride (0.9 g.) in ether (55 ml.). The reduction and recovery procedures were carried out as previously described and the glycoside of the neutral disaccharide was recovered as a porous solid (358 mg.). Hydrolysis with *N* sulphuric acid (10 ml.) on a boiling-water bath yielded two sugars, a monomethyl pentose and a trimethyl hexose as shown by chromatographic examination in solvents B and C. The sugars were separated on a Celite column using butanol saturated with water as the solvent.

*Identification of 3-O-methyl-*D*-xylose.*—The R_g value of the monomethyl pentose in solvent B corresponded to that of an authentic sample of 3-*O*-methyl-D-xylose. Anal.: calculated for $C_6H_{12}O_5$: OCH_3 19.9%; found: OCH_3 18.6%. The sirup, which did not crystallize, had $[\alpha]_D^{25}$ +18°±1° (*c*, 1.0% in water), reported value +19° (9). Preparation of the osazone yielded crystalline 3-*O*-methyl-D-xylosazone, m.p. 170°–171° C. (reported value 172° C. (3)).

*Identification of 2,3,4-tri-O-methyl-*D*-glucose.*—The trimethyl hexose (233 mg.) had the same R_g values (0.78 and 0.53) in solvents B and C respectively as an authentic sample of 2,3,4-tri-*O*-methyl-D-glucose, and $[\alpha]_D^{25}$ +68°±2° (*c*, 1.0% in water), reported value +66.8° (14). Anal.: calculated for $C_9H_{18}O_6$: OCH_3 41.9%; found: OCH_3 41.6%. The trimethyl glucose (95 mg.) was oxidized with nitric acid (10 ml.; *d*, 1.2) for 2.5 hours at 90° C. After removal of solvents by distillation with water and ethanol, the recovered sirup was converted to the corresponding lactone by heating for 3 hours at 90° C. *in vacuo* and to the methyl ester by refluxing with 2% methanolic hydrogen chloride for 6 hours. The methyl ester of the lactone (89 mg.) was distilled and 2,3,4-tri-*O*-methyl-D-glucosaccharo-1,5-lactone-6-methyl ester was recovered, yield 47 mg., b.p. (bath temperature) 140°–150° C. at 0.01 mm. The product crystallized readily on nucleation, m.p. 105°–106° C., unchanged on admixture with an authentic sample, and had $[\alpha]_D^{25}$ +54°±2° in 20 hours (*c*, 1% in methanol). Anal.: calculated for $C_{10}H_{16}O_7$: OCH_3 50.0%; found: OCH_3 50.4%.

Fraction II.—This sirup had the same R_g values (0.59–0.60 and 0.67–0.68) in solvents D and A respectively as an authentic sample of 3-*O*-methyl-D-xylose. This sirup crystallized, and recrystallization from methanol yielded 3-*O*-methyl-D-xylose, m.p. 103°–104° C., unchanged on admixture with an authentic sample, $[\alpha]_D^{25}$ +18°±1°. Anal.: calculated for $C_6H_{12}O_5$: OCH_3 18.9%; found: OCH_3 18.6%.

Fraction III.—This material was recovered from the Celite column as a clear, white sirup which had $[\alpha]_D^{25}$ +23°±1°, η_D^{25} 1.4732, OCH_3 34.8% (calculated for $C_7H_{14}O_5$: OCH_3 34.8%). The R_g value in solvent B (0.67–0.68) was identical with that of an authentic sample of 2,3-di-*O*-methyl-D-xylose. The crystalline aniline derivative, 2,3-di-*O*-methyl-*N*-phenyl-D-xylosylamine, was prepared having m.p. and mixed m.p. 123°–124° C.

Fraction IV.—This sirup partially crystallized on standing. Recrystallization from ethyl ether containing a small amount of petroleum ether yielded 2,3,4-tri-*O*-methyl-D-xylopyranose, m.p. 89–90° C., unchanged on admixture with an authentic sample, $[\alpha]_D^{25}$ +21°±1° (*c*, 1.0% in water), OCH_3 48.1% (calculated for $C_8H_{16}O_5$: OCH_3 48.4%). The R_g value (0.86–0.88) in solvent C was identical with that of 2,3,4-tri-*O*-methyl-D-xylose.

Further Examination of Uronic Acid Component

A portion of the main uronic acid fraction (678 mg.) as isolated earlier was converted

to its methyl glycoside methyl ester by refluxing with 2% methanolic hydrogen chloride (25 ml.) for 8 hours. The methyl glycoside methyl ester of the aldobiouronic acid (654 mg.) in tetrahydrofuran (45 ml.) was reduced by dropwise addition to a solution of lithium aluminum hydride (700 mg.) in tetrahydrofuran (35 ml.). The glycoside of the neutral disaccharide was recovered as foamed solid (583 mg.).

Methylation of the Disaccharide

The 4-*O*-methyl-D-glucosyl-D-xylose (583 mg.) was dissolved in 20% sodium hydroxide (10 ml.) and methylated by the simultaneous dropwise addition of 40% sodium hydroxide (55 ml.) and dimethyl sulphate (30 ml.) at room temperature. The methylation was repeated once. The solution was heated at 95° C. for 1 hour, cooled, acidified with 2 *N* sulphuric acid to pH 5.0, and extracted continuously with chloroform for 24 hours. Evaporation of the chloroform yielded a sirup (430 mg.). Two further methylations with Purdie's reagents (silver oxide 10 g., and methyl iodide 30 ml.) yielded a clear sirup (391 mg.), $[\alpha]_D^{25}$ +112°±1° (*c*, 1.0% in chloroform). The infrared spectrum indicated that there were no free hydroxyl groups. Anal.: calculated for $C_{18}H_{34}O_{10}$: OCH_3 52.9%; found: OCH_3 51.2%.

Hydrolysis of fully methylated disaccharide and recovery of sugar components.—The methylated disaccharide (391 mg.) was hydrolyzed by heating for 18 hours in 8% methanolic hydrogen chloride (25 ml.), and after removal of the solvent, by further heating for 10 hours at 100° C. with 0.5 *N* hydrogen chloride. The hydrolyzate was neutralized by silver carbonate, deionized by Amberlite IR-120 and Amberlite IR-45, and concentrated to a sirup (280 mg.). Chromatographic examination of the sirup in solvent B showed two sugars corresponding to 3,4-di-*O*-methyl-D-xylose and 2,3,4,6-tetra-*O*-methyl-D-glucose. The sugars were separated on a Celite column (10) using butanol saturated with water as the solvent to give 3,4-di-*O*-methyl-D-xylose (90 mg.) and 2,3,4,6-tetra-*O*-methyl-D-glucose (123 mg.).

Identification of 3,4-di-O-methyl-D-xylose.—The colorless sirup had $[\alpha]_D^{25}$ +19°±1° (*c*, 1.4% in water). On chromatographic examination in solvent C it had an R_g value of 0.38 and thus was distinguishable from 2,3-di-*O*-methyl-D-xylose (R_g 0.31) and 2,4-di-*O*-methyl-D-xylose (R_g 0.27). Anal.: calculated for $C_7H_{14}O_5$: OCH_3 34.8%; found: OCH_3 34.8%. A solution of the 3,4-di-*O*-methyl-D-xylose (75 mg.) in water (1.2 ml.) containing barium carbonate (60 mg.) was oxidized by bromine (0.6 ml.) in the dark for 60 hours. The bromine was removed by aeration with nitrogen, and the solution was acidified by *N* hydrochloric acid, filtered, and extracted continuously with chloroform for 72 hours. The recovered sirup from the chloroform extraction was heated *in vacuo* at 90° C. for 3 hours to lactonize the acid. On seeding with 3,4-di-*O*-methyl-D-xylono-δ-lactone, crystallization took place. Recrystallization from ether containing hexane yielded 3,4-di-*O*-methyl-D-xylono-δ-lactone, m.p. 66°–67° C., $[\alpha]_D^{25}$ −22°±1° (*c*, 1.1 in water).

Identification of 2,3,4,6-tetra-O-methyl-D-glucose.—The sugar as recovered from the Celite column crystallized spontaneously on removal of solvent. Recrystallization from ether – petroleum ether solution yielded white needles, $[\alpha]_D^{25}$ +82°±2° (in water), m.p. and mixed m.p. 96° C. The 2,3,4,6-tetra-*O*-methyl-D-glucose (90 mg.) in methanol (3 ml.) containing aniline (3 ml.) was refluxed for 2.5 hours. On removal of solvent the anilide crystallized at once. Recrystallization from ethanol yielded 2,3,4,6-tetra-*O*-methyl-*N*-phenyl-D-glucosylamine, m.p. 116°–117° C., $[\alpha]_D^{25}$ +205°±1° (*c*, 1.1% in acetone).

Estimation of Degree of Polymerization

Viscosity measurements.—Viscosity determinations were made on solutions of beechwood hemicellulose in 0.1 *M* sodium chloride and cupriethylenediamine. Solution concentrations were within the range 0.20–1.00% and measurements were made in Oswald-Cannon-Fenske viscometers in a water bath at 25°±.02° C. Weight average molecular weights were calculated by substituting limiting viscosity number $[\eta]$ values in Staudinger's equation using 5.0×10^{-5} as the value for K_m as proposed by Husemann (8). The molecular weights obtained for the hemicellulose in both solvents were 6000–6200, which corresponds to a D.P. of 46–47.

Reducing power.—Samples of the beechwood hemicellulose (50 mg.) were oxidized by alkaline hypoiodite according to the method of Chanda *et al.* (5). Number average molecular weights based on reducing power of the hemicellulose gave values between 6200 and 6700, which corresponds to one reducing end group for each 47–51 sugar units.

Periodate oxidation.—Beechwood hemicellulose (100 mg.) was oxidized by 1% sodium metaperiodate (100 ml.) in the dark at 16°. Analyses for periodate consumption and formic acid production were made at 24 hour intervals (5). The results showed that the oxidation was essentially complete in 144 hours and that 0.98 moles of periodate had been consumed per mole of anhydropentose unit and 0.09 moles of formic acid had been produced per mole of sugar.

ACKNOWLEDGMENT

The author gratefully acknowledges the valuable technical assistance of A. E. Castagne.

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MECHANISM OF THE DECOMPOSITION OF ETHYLENE WHEN PHOTOSENSITIZED BY METAL VAPORS[1]

E. WHALLEY

ABSTRACT

A detailed mechanism of the molecular split of ethylene into acetylene and hydrogen, which occurs when ethylene is photosensitized by $Hg(^3P_1)$, is presented. It is suggested that the triplet ethylene molecule which is first formed isomerizes to a molecule of uncertain lifetime in which two hydrogen atoms act as "bridges" between the two carbon atoms. The hydrogen molecule which splits from the ethylene molecule is formed when these two atoms leave simultaneously. The experimental observations on the decomposition of ethylene when photosensitized by $Cd(^1P_1)$ or $Zn(^1P_1)$ are consistent with the primary interaction of the excited metal atom with either a C–H group or with the π electrons.

1. INTRODUCTION

Electronically excited metal atoms are quenched by olefins very much more readily than by paraffins (10).[2] In olefins there are three kinds of electrons involved in chemical bonding, viz. σ_{C-C}, σ_{C-H}, and π_{C-C}. Paraffin hydrocarbons contain σ_{C-C} and σ_{C-H} electrons, and have very low quenching cross-sections; hence, it is provisionally concluded that the interaction of the π_{C-C} electrons with the excited metal atom is responsible for the large quenching by olefins. The primary process is

$$C_2H_4 + M^* \rightarrow C_2H_4^* + M,$$

where M represents the metal atom, and the superscript asterisk denotes a state excited electronically or vibrationally (this includes rotational excitation) or in both modes.

The fate of the activated molecule $C_2H_4^*$ depends upon the properties of the excited atom M*, particularly on its multiplicity and its energy. These properties determine the properties of $C_2H_4^*$, particularly whether either the electronic or the vibrational degrees of freedom, or both, are excited (7). If M* is $Na(^2P)$ and M is $Na(^2S)$, $C_2H_4^*$ is a vibrationally excited molecule in its electronic ground state. It has insufficient energy to react and it loses its energy by collisions until it reaches thermal equilibrium. If M* is $Cd(^3P_1)$ or $Zn(^3P_1)$ and M is $Cd(^1S_0)$ or $Zn(^1S_0)$ the excited ethylene must be in its first triplet state according to the Wigner–Witmer correlation rules and reasonable speculations about the energy of the first triplet state (see Ref. 7). It also appears to have insufficient energy to decompose (10), and it loses its electronic and vibrational energy at an unknown rate by collisions.

If M* is $Hg(^3P_1)$ and M is $Hg(^1S_0)$ the resulting excited ethylene is again a vibrationally excited triplet, presumably in the same electronic state as that from $Cd(^3P_1)$ or $Zn(^3P_1)$, but with more vibrational energy. It now has sufficient energy to decompose, and the total reaction is

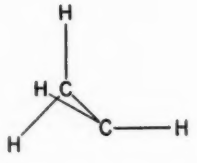
$$C_2H_4 + Hg(^3P_1) \rightarrow C_2H_2 + H_2 + Hg(^1S_0).$$

It is well verified that this reaction occurs via an excited molecule, and a detailed mechanism for the reaction is proposed in this paper. If M* is $Cd(^1P_1)$ or $Zn(^1P_1)$ and M is $Cd(^1S_0)$ or $Zn(^1S_0)$ it is not known whether or not an excited molecule mechanism is followed, and possible mechanisms are briefly discussed.

[1]*Manuscript received March 5, 1957.*
Contribution from the Division of Applied Chemistry, National Research Council, Ottawa.
Issued as N.R.C. No. 4333.
[2]*Unless otherwise stated, experimental information quoted in this paper is taken from Reference (10).*

2. ETHYLENE

We first consider the structure of the excited ethylene molecules. Those obtained from triplet atoms are in the first excited triplet state. This almost certainly is obtained by the uncoupling of the spins of the π electrons and their localization, one on each carbon atom. The structure of this molecule has been discussed by Walsh (11) and he concludes that the carbon valencies are pyramidally directed, and the ground state is staggered, thus:



More detailed calculations (6, 8) confirm that the methyl radical is probably pyramidal, but almost planar, and this is confirmed spectroscopically by Herzberg and Shoosmith (5). This indirectly confirms the structure of triplet C_2H_4. The energy transferred from the $Hg(^3P_1)$ is 471 kj. mole^{-1} (112.6 kcal. mole^{-1}). The energy absorbed in the excitation of ethylene from its ground state to its first triplet state is not known, but it is likely to be not more than about 100–200 kj. mole^{-1} (20–40 kcal. mole^{-1}). The triplet ethylene has, therefore, considerable vibrational energy.

It seems to be well verified that the excited molecule decomposes homogeneously and intramolecularly. The claim of Darwent (4) that a large amount of decomposition occurs at the wall appears to be incorrect (2). Cvetanović and Callear (3) have shown conclusively by using ethylene labelled with deuterium that the reaction occurs completely intramolecularly, and this has been confirmed by Lossing *et al.* (9) by mass spectrometry. Darwent (4) and Callear and Cvetanović (1) have shown that the kinetics are not in accordance with the simple reaction mechanism (10)

$$\begin{aligned} C_2H_4 + Hg(^3P_1) &\rightarrow C_2H_4^* + Hg(^1S_0), \\ C_2H_4^* + C_2H_4 &\rightarrow 2C_2H_4, \\ C_2H_4^* &\rightarrow C_2H_2 + H_2, \end{aligned}$$

and Callear and Cvetanović show that they do agree with a mechanism in which the triplet ethylene which is first formed cannot decompose directly to acetylene and hydrogen but must first isomerize to another excited ethylene $C_2H_4^{**}$ which can so decompose. The complete scheme is

$$\begin{aligned} C_2H_4 + Hg(^3P_1) &\rightarrow C_2H_4^* + Hg(^1S_0), & k_1 \\ C_2H_4^* &\rightarrow C_2H_4^{**}, & k_2 \\ C_2H_4^{**} &\rightarrow C_2H_4^*, & k_3 \\ C_2H_4^* + C_2H_4 &\rightarrow 2C_2H_4, & k_4 \\ C_2H_4^{**} + C_2H_4 &\rightarrow 2C_2H_4, & k_5 \\ C_2H_4^{**} &\rightarrow C_2H_2 + H_2. & k_6 \end{aligned}$$

The isomerization of $C_2H_4^{**}$ to $C_2H_4^*$ was not included in the original scheme and we shall show that the measured rates indicate that it has little influence on the course of the reaction.

It is possible to invent more elaborate sets of reactions with more rate constants, and so to improve agreement with experiment by introducing more parameters; the set above appears to be the simplest. A steady state treatment of the above reactions shows

that the rate of production of hydrogen R_{H_2} depends upon the intensity of light absorbed I_a and the partial pressure of ethylene p, in the manner

[1] $$I_a/R_{H_2} = 1 + Ap + Bp^2,$$

where

[2] $$A = \left(1+\frac{k_3}{k_6}\right)\frac{k_4}{k_2}+\frac{k_5}{k_6},$$

[3] $$B = \frac{k_4}{k_2}\frac{k_5}{k_6}.$$

Callear and Cvetanović (1) have shown that if $R_{H_2}^{-1/2}$ is plotted against p a nearly straight line is obtained. This means that approximately

[4] $$A^2 = 4B.$$

Equations [2], [3], and [4] contain five unknowns, viz. A, B, $k_3/k_6=x$, $k_4/k_2=y$, and $k_5/k_6=z$. There are therefore two degrees of freedom. It is a rather remarkable property of these equations that there is only one possible value of x consistent with the condition that x, y, and z must be real, positive numbers. By inserting equation [2] and [3] into [4] we find that

[5] $$(1+x)^2y^2-2z\,(1-x)y+z^2 = 0.$$

Solving for y we find that

[6] $$\frac{y}{z} = \frac{(1-x)\pm 4(-x)^{\frac{1}{2}}}{(1+x)^2}.$$

Since x, y, and z must be real and positive, the only possible solution of [6] is

$$x = 0, \qquad y = z.$$

Hence the kinetics show that

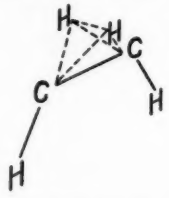
[7] $$k_3/k_6 \ll 1,$$
$$k_4/k_2 = k_5/k_6 \text{ very nearly.}$$

This means that C_2H_4** decomposes much faster than it isomerizes to C_2H_4*. Conditions [7] were suggested by Callear and Cvetanović.

We know the probable structure of C_2H_4* and the question immediately arises, what is the nature of C_2H_4**? Callear and Cvetanović (1) showed that when *cis*-$C_2H_2D_2$ was photosensitized by $Hg(^3P_1)$ it isomerized to both *trans*-$C_2H_2D_2$ and *anti*-$C_2H_2D_2$ in at least one of the deactivation processes. This must occur by migration of at least two hydrogen atoms. The migrations can occur either separately or together. If one hydrogen atom migrates to the other carbon, triplet ethylidene CH_3CH is produced. The two unshared, unpaired electrons on one carbon atom repel one another more than they would if they were on different atoms and so the electronic energy of CH_3CH is higher than that of CH_2CH_2. To produce this extra electronic energy an equivalent amount of vibrational energy must be concentrated in those modes which lead to a shift of one hydrogen atom. Less vibrational energy need be converted to electronic energy if two hydrogen atoms move simultaneously. Also it would be quite strange if ethylidene were to split off a hydrogen molecule; it would be more likely that a C—H split would occur as for example occurs in the mercury photosensitized decomposition

of substituted ethylenes (9, 10). It is quite easy to see, as we show below, how a molecular split can occur if two hydrogen atoms move together. We conclude therefore that simultaneous migration is more likely than consecutive migration.

The state halfway along this simultaneous shift of the H atoms is



and it is proposed that this molecule is C_2H_4**. Each C—H—C bond in the bridge is a three electron three center bond, and it is not likely to be very stable. The hydrogens in the bridge will interact with one another as indicated by the dotted lines joining them. The same structure can be considered as a hydrogen molecule embedded in the π electrons of triplet acetylene. It is immediately evident that it will have a strong tendency to decompose to a hydrogen molecule and a triplet acetylene molecule. The kinetics indicate that it decomposes, and is deactivated by collisions, but that it rarely isomerizes spontaneously to C_2H_4*.

The mechanism of the $Cd(^1P_1)$ or $Zn(^1P_1)$ photosensitized reaction is not so clear cut. The main reaction is undoubtedly a split of a C—H bond to give an H atom and a C_2H_3 radical (10). There are two possible mechanisms, corresponding respectively to interaction of the excited metal atom with either the σ_{C-H} or the π_{C-C} electrons. These may be written

$$C_2H_3\text{—}H + Cd(^1P_1) \rightarrow C_2H_3 \ldots H \ldots Cd \rightarrow C_2H_3 + H + Cd(^1S_0) \text{ or } CdH,$$

and

$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + Cd(^1P_1) \rightarrow \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} \cdots Cd \rightarrow \begin{matrix} CH_2^* \\ \| \\ CH_2 \end{matrix} + Cd(^1S_0),$$

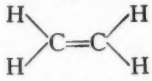
$$\begin{matrix} CH_2^* \\ \| \\ CH_2 \end{matrix} \rightarrow C_2H_3 + H.$$

The experimental evidence is insufficient to decide between these two mechanisms. Quenching is not observed, but this may be because the lifetime of C_2H_4* is short compared with the time between collisions even at the highest pressures studied.

Laidler (7) has suggested in effect that the primary interaction is with the σ_{C-H} electrons, the first mechanism above, because it appeared to be difficult otherwise to account for the difference between the molecular and the radical decomposition of the excited molecules. It is not wholly satisfactory to postulate that $Cd(^1P_1)$ and $Zn(^1P_1)$ interact with σ_{C-H} electrons while $Na(^2P)$, $Cd(^3P_1)$, $Zn(^3P_1)$, and $Hg(^3P_1)$ interact with the relatively much more extensive π_{C-C} electrons. There is no other evidence for this, and it is possible, as we show below, to account for the different modes of decomposition of the excited molecules. Consequently, the experimental evidence is consistent with an excited molecule mechanism, but an interaction with σ_{C-H} is not excluded.

If an excited ethylene molecule is produced by interaction with $Cd(^1P_1)$ or $Zn(^1P_1)$ it must be in a singlet state, and since there is no excited singlet level with sufficiently low energy, it must be in its electronic ground state. The energy transferred from the

excited metal atom must be converted to vibrational energy. The structure is, therefore,



and it will be relatively difficult for this molecule to reach the singlet state of the bridge structure; consequently conditions are not favorable for an intramolecular split of a hydrogen molecule. The relative probability of the alternative mode, a split of a C—H bond, is therefore increased, and little, if any, molecular decomposition occurs.

It is interesting that at temperatures of about 300° there is evidence that triplet ethylene obtained by photosensitization with $Hg(^3P_1)$ decomposes to a small extent by a C—H split. Evidently the higher vibrational energy which the molecule possesses increases somewhat the chance of a C—H split.

ACKNOWLEDGMENT

The author is greatly indebted to Dr. R. J. Cvetanović, who drew his attention to this problem, for discussion.

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NOTES

THE KINETICS OF THE THERMAL DECOMPOSITION OF DIMETHYL-2,2′-BIS-AZO-ISOBUTYRATE[1]

J. S. MACKIE[2] AND S. BYWATER

The kinetics of the thermal decomposition of bis-azo-nitriles has received much attention in late years. Less work has been presented on the decomposition of the corresponding azo esters. The kinetics of the thermal decomposition of dimethyl-2,2′-bis-azo-isobutyrate has been followed gasometrically by Lewis and Matheson (3) and by Ziegler *et al.* (5). The final products are described by Bickel and Waters (1).

EXPERIMENTAL

Dimethyl-2,2′-bis-azo-isobutyrate (AIB) was prepared from 2,2′-bis-azo-isobutyronitrile (Westville Laboratories) by the method reported by Thiele and Heuser (4). It was purified by recrystallization from ether to a melting point of 30°. The solvent used was 2,2,5-trimethylhexane (Phillips Petroleum Co., purity >95%). This was freed from polar and unsaturated compounds by passage through a silica gel column until optically clear to 250 mμ. The kinetic measurements of the rate of decomposition were made using the technique previously reported (1) using measurements of optical density at 390 mμ. The purified azo compound was found to have a symmetrical absorption band with maximum at 360 mμ; $E_{max} = 18.0$. Measurements of change in optical density with time were also made at 270, 280 mμ where the absorption of the azo compound is negligible.

RESULTS

The thermal decomposition in purified nitrogen (2) was followed at 70°, 80°, 90°, and 100° C. and normally at concentrations of 0.03, 0.06, and 0.10 molar azo compound. The decomposition followed first order kinetics as far as the reaction was measured (normally over 90% decomposition). The first order constants were independent of initial concentration of AIB. Rate constants obtained are shown in Table I.

TABLE I

T (° C.)	70	80	90	100
$k_1 \times 10^4$ (sec.$^{-1}$)	0.223	0.786	2.59	8.45

The experimental results are best fitted by the relation k_1 (sec.$^{-1}$) $= 1.31 \times 10^{15} \exp(-31.1/RT)$. Lewis and Matheson (3) report $k_1 = 1.09 \times 10^{-4}$; $E = 35.8$ (xylene, 80°). Ziegler, Deparade, and Meye give $k_1 = 1.04 \times 10^{-4}$ (undecane, 80°); $k_1 = 1.61 \times 10^{-4}$, (nitrobenzene, 80°); $k_1 = 17.3 \times 10^{-4}$ (nitrobenzene, 100°); $E = 30.9$. There are no indications in either paper that measurements were made at enough temperatures for an accurate activation energy assessment.

[1]*Issued as N.R.C. No. 4324.*
[2]*N.R.L. Postdoctoral Fellowship holder, 1954–56.*

At 270, 280 mμ the optical density *increased* with time to an almost steady value at 70° and 80°, and at higher temperatures increased to a maximum and then slowly decreased. This is similar to the observations on the azonitrile (2). The optical density values are such that this cannot be accounted for by any of the reported products (1) and must indicate the formation of some other compound, thermally unstable at higher temperatures.

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RECEIVED FEBRUARY 21, 1957.
APPLIED CHEMISTRY DIVISION,
NATIONAL RESEARCH COUNCIL,
OTTAWA, CANADA.

THE INTRINSIC VISCOSITIES OF AQUEOUS SOLUTIONS OF SMALL MOLECULES

J. T. EDWARD

For finite concentrations of neutral spheres suspended in a liquid, the Einstein equation for specific viscosity η_{sp} is modified to the power series

$$\eta_{sp}/\phi = \alpha_0+\alpha_1\phi+ \ldots , \quad [1]$$

where ϕ is the volume fraction occupied by the spheres, and α_0 and α_1 are constants equal to 2.5 and about 13 respectively (3, 7, 8, 11, 12, 19). While this equation is derived from classical hydrodynamic principles, and hence has no necessary validity for solutions in which the size of the solute approaches that of the solvent molecule, Vand (19) found it applicable to aqueous solutions of sucrose if one assumed some hydration of the sucrose molecule. However, in default of any means of estimating the volume of the sucrose molecule, Vand's treatment was indirect and involved.

Recently a simple means of estimating the van der Waals volume V_w of a molecule has been described (5). In aqueous solution this volume will be multiplied by a hydration factor H, and hence the volume fraction occupied by the hydrated molecules in a solution having a concentration of c g./100 ml. will be given by

$$\phi = cNV_wH/100M, \quad [2]$$

M being the molecular weight of the solute and N Avogadro's number. The intrinsic viscosity $[\eta]$ of the solution will then be given by

$$[\eta] = \lim_{c\to 0} \eta_{sp}/c = \alpha_0 NV_wH/100M. \quad [3]$$

In applying this equation to actual molecules, it is necessary to take some account of their shapes, since for all non-spherical shapes $\alpha_0 > 2.5$. For solute particles having ellipsoidal shapes, α_0 may be calculated from the ratios of the axes of the ellipsoids by

Simha's equations (16). The shapes and axial ratios of the molecules shown in Table I were determined by inspection and measurement of models of the compounds built with the Courtaulds' accurately-scaled atomic models (9, 14). In cases where several different

TABLE I

HYDRATION FACTORS ESTIMATED FROM INTRINSIC VISCOSITIES (H_η) AND FROM DIFFUSION COEFFICIENTS (H_D)

Compound	Shape[a]	Axial ratio	H_η	Ref.[b]	H_D	Ref.[c]
1. Pentaerythritol	sph	1.00	2.1 (20°)	(13)	1.8 (20°)	(13)
2. Glucose	obl	1.81	1.5 ,,	(13)	2.2 ,,	(13)
3. Sucrose	pro	2.04	1.7 ,,	(13)	2.4 ,,	(13)
4. Valine	obl	1.43	2.4 ,,	(13)	2.2 ,,	(13)
5. β-Alanine	pro	2.00	1.4 ,,	(13)	1.6 ,,	(13)
6. α-Alanine	obl	1.21	1.8 ,,	(13)	1.9 ,,	(13)
7. Glycine	pro	1.70	0.9 ,,	(13)	1.5 ,,	(13)
8. Phenol	obl	2.03	0.6 (25°)	(18)	1.1 (18°)	(17)
9. Hydroquinone	pro	1.76	0.7 ,,	(18)	1.2 (20°)	(17)
10. Recorcinol	obl	2.23	1.0 ,,	(18)	1.4 ,,	(17)
11. Glycerol	pro	1.80	1.5 ,,	(15)	1.4 ,,	(17)
12. Urethane	pro	2.00	1.3 (10°)	(2)	0.9 (18°)	(17)

[a]sph = *sphere;* pro = *prolate ellipsoid;* obl = *oblate ellipsoid.*
[b]*Literature source of viscosity data.*
[c]*Literature source of diffusion coefficients.*

conformations of the molecule were possible, by rotation about single bonds, the most extended conformation was chosen (1, 10). The effect of hydration on the shape of the molecule was ignored.

The hydration factors (H_η) calculated from equation [3] using these values of α_0 are shown in Table I. The intrinsic viscosities of aqueous solutions of compounds 1–7 have been given by Polson (13), those of compounds 8–12 were obtained from plots of η_{sp}/c against c, using data from the literature. Except in the case of glycerol, there was a fairly wide scatter of the experimental points from a straight-line plot, and hence the values of H_η for these compounds must be accepted with reserve.

The values of the hydration factor obtained in this way are of the same magnitude as the values (H_D in Table I) obtained from diffusion coefficients D in water by use of the modified Stokes–Einstein equation (6):

$$D = \frac{kT}{5\pi\eta_0}\left(\frac{f_0}{f}\right)\left(\frac{4\pi}{3V_w H}\right)^{\frac{1}{3}}, \qquad [4]$$

where k is Boltzmann's constant, T is the temperature, η_0 the viscosity of water, and (f/f_0) the frictional ratio (4) to correct, where necessary, for the non-spherical shape of the molecule. The values of H_η and H_D have not in all cases been calculated for the same temperature, but the differences are too small to affect grossly the comparison (1). Consequently, it would appear that equation [1] is applicable to the specific viscosities of quite small molecules in aqueous solution. However, it should be emphasized that equations [1] and [4] have empirical validity only, and that no precise meaning should be attached to the hydration factors, which probably measure several different solvent effects.

A knowledge of the hydration factor enables one to calculate ϕ for a given concentration of solute by equation [2]. A plot of η_{sp}/ϕ against ϕ for glycerol (15), using $H = 1.54$, gave a good straight-line curve from which a value of 6.75 for α_1 in equation [1] was

obtained. This value is considerably lower than that found in studies of aqueous suspensions of polystyrene latex particles (diameter ≈2600 Å) (3) and of glass spheres (diameter ≈50,000 Å) (11). However, Vand (19) has given reasons for expecting this constant to decrease as the suspended particles approach molecular dimensions.

I am most grateful to Dr. D. A. I. Goring for a discussion of this topic.

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Received March 1, 1957.
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IODINE COMPLEXES IN INERT SOLVENTS. VII. THERMODYNAMIC CONSTANTS AND SPECTROSCOPIC DATA FOR THE REACTION $2I_2 \rightleftharpoons I_4$ IN CARBON TETRACHLORIDE

P. A. D. de Maine*

Some workers (2, 7) have reported that the weak absorption band, with center near 2800 Å, found for iodine dissolved in carbon tetrachloride arises from contributions by two absorption bands. One is due to I_2 (with center near 2775 Å), and the other is due to I_4 (with center near 2880 Å (7) or 2935 Å (2)). These workers have used an approximate method for estimating $K\epsilon_{I_4}$ (K is the equilibrium constant for the reaction $2I_2 \rightleftharpoons I_4$; ϵ_{I_4} is the molar extinction coefficient for I_4). The heat of formation of I_4 in carbon tetrachloride ($\Delta H = -1.0$ (7) or -1.96 (2) kcal. per mole) has been estimated in both cases from $K\epsilon_{I_4}$ with the assumption that ϵ_{I_4} does not alter with changes in temperature.

de Maine, de Maine, and Goble (5) have used an exact method to obtain K, ϵ_D, and ϵ_M (D is dimer; M is monomer) for the reaction

$$2MeNO_2 \overset{K}{\rightleftharpoons} (MeNO_2)_2,$$

where the $MeNO_2$ and the dimer bands are superimposed, in carbon tetrachloride. These

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authors found that a system of this kind is described by the following exact equations:

$$[1] \qquad D_{obs}/(C_A - C) = 2K\epsilon_D(C_A - C) + \epsilon_M,$$

$$[2] \qquad C_A^2/D_D = 1/2K\epsilon_D + (2C_A - C)/\epsilon_D,$$

$$[3] \qquad C = [1 + 4KC_A - (1 + 8KC_A)^{\frac{1}{2}}]/4K,$$

where C_A is the total concentration of nitromethane (as $MeNO_2$), $C/2$ is the concentration of $(MeNO_2)_2$, D_{obs} is the measured optical density, and D_D is the optical density of the dimer species.

D_{obs} and C_A were measured, and exact values for K, ϵ_D, and ϵ_M were obtained from equations [1], [2], and [3] by a method of successive approximations.

The exact method just described has been applied to data for the carbon tetrachloride – iodine solutions ($C_A = 12\times10^{-3}$ to 0.8×10^{-3} moles per liter) near 17° C., to obtain accurate values for K (= 2.28 liters/mole), ϵ_D, and ϵ_M. Molar extinction coefficients for I_2 (ϵ_M) and I_4 (ϵ_D) in carbon tetrachloride at 17° C. are given in Table I. The values

TABLE I

MOLAR EXTINCTION COEFFICIENTS FOR I_2 AND I_4 DISSOLVED IN CCl_4, NEAR 17° C.; ϵ_{I_2} AND ϵ_{I_4} REFER TO VALUES OBTAINED BY THE NEW METHOD, ϵ_{I_2}' ARE THE FIRST-APPROXIMATION VALUES AT 20° C. REPORTED BY DE MAINE (2)

Wavelength in mμ	ϵ_{I_4}	ϵ_{I_2}	ϵ_{I_2}'
285	363	46.9	49.0
290	389	43.5	44.8
295	384	39.2	—
300	379	34.7	36.5
310	329	26.3	26.2
320	263	19.1	19.5
330	152	16.1	15.6
340	52	14.2	12.6
350	42	11.3	12.0
360	14	10.0	—
370	12	8.3	8.3
380	0	7.1	7.1

for ϵ_M are also compared to the approximate values reported earlier (2). The shapes of both molar extinction curves, calculated by the exact method, are given in Fig. 1.

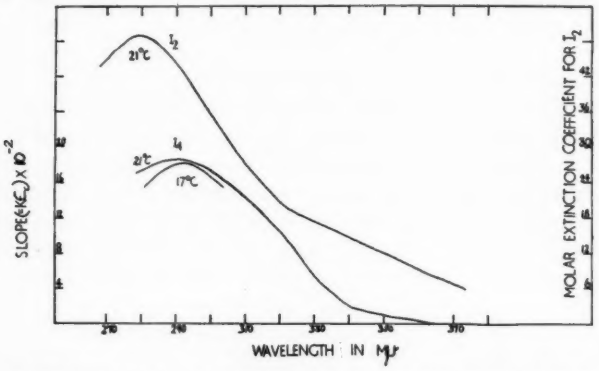

FIG. 1. Shapes of the molar extinction curves for I_2 and I_4 in carbon tetrachloride at 17° C. and 21° C.

The shapes of the curves are not appreciably different from the corresponding first-approximation curves (Ref. 2, Fig. 2). This means that the band centers reported earlier (2) are correct. It was also found that the I_4 absorption band, with center near 2935 Å, does not extend to the longer wavelength side of 3700 Å.

The accurate value obtained for the equilibrium constant (K = 2.28 liters/mole at 17° C.) corresponds to a free energy change of $\Delta F = -1.81$ kcal. per mole at 25° C. Corresponding ΔS values, calculated by means of the equation $\Delta F = \Delta H - T\Delta S$, using $\Delta H = -1.96$ (2) or -1.0 (7) kcal. per mole, are given in Table II. These values for

TABLE II

ΔF AND ΔS FOR THE REACTION $2I_2 \rightleftharpoons I_4$ IN CCl_4 (25 IS THE REFERENCE STATE); $\Delta F = -RT \ln K_x$, $\Delta F = \Delta H - T\Delta S$, WHERE K_x IS THE EQUILIBRIUM CONSTANT IN MOLE FRACTION UNITS

ΔF, kcal.	ΔS, e.u.	ΔH, kcal.	K at 25° C., liters/mole
−1.81	−0.50	−1.96	2.05
−1.84	+2.81	−1.0	2.16

ΔF, ΔH, and ΔS, together with the corresponding values for the iodine complexes with pyridine (10), diethyl ether, methanol, or ethanol (3), do not fit the empirical relationships of Andrews and Keefer (1). This supports the author's view (3) that the linear relationship between ΔF and ΔS or ΔH applies only for donor molecules with similar molecular shapes.

Comparison of the extinction coefficients at the absorption maximum (ϵ_{max}), and the heat of formation (ΔH) or equilibrium constant (K) for the reaction $2I_2 \rightleftharpoons I_4$, with corresponding constants for some other complexes of iodine in carbon tetrachloride (Table III) shows that there is no simple relation between the constants. Mulliken's

TABLE III

THERMODYNAMIC AND SPECTROSCOPIC DATA FOR SOME IODINE COMPLEXES IN CARBON TETRACHLORIDE; K IS THE EQUILIBRIUM CONSTANT IN MOLE FRACTION UNITS AT 25° C., ϵ_e AND ϵ_{vis} ARE THE MOLAR EXTINCTION COEFFICIENTS FOR THE CHARGE TRANSFER AND VISIBLE BANDS AT THEIR ABSORPTION MAXIMA (λ_e AND λ_{vis})

Donor	λ_e	ϵ_e	λ_{vis}	ϵ_{vis}	ΔF	ΔH	ΔS	K
I_2	2935	390	–	–	−1.81	−1.96	−0.50	21.3
MeOH[3]	2428	8360	4400	973	−0.91	−1.90	−3.32	4.6
EtOH[3]	2433	10802	4430	1082	−0.83	−2.10	−4.09	4.0
Et_2O[3]	2490	4700	4680	873	−1.31	−4.30	−9.86	8.7

"charge-transfer" theory (8) predicts that ϵ_{max} (or more exactly the integral extinction for the band) should increase with ΔH or K, and that K should increase with ΔH. The lack of the expected correlation cannot be attributed to neglect of activities of the reaction components (4). Finally Mulliken's new "charge-transfer – contact charge-transfer" theory (9), which is based on the experimental work of Evans (6) with iodine-saturated paraffin solutions, cannot explain why the visible absorption band is located nearer the ultraviolet when K and ΔH are smaller for the iodine-oxygenated compound complexes (4). It is therefore concluded that neither the simple "charge-transfer" nor the new "charge-transfer – contact charge-transfer" theory explains all the experimental data for the iodine complexes mentioned.

The author is deeply indebted to Professor W. C. Price of King's College for providing facilities for the experimental work and calculations. Attention should again be drawn to the fact that the method used in the analysis was developed by the author from a method suggested by Dr. E. W. Kosower through a private communication.

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RECEIVED NOVEMBER 30, 1956.
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THE DECOMPOSITION OF 1-BUTENE AND 1-BUTENE-4-d_3 INDUCED BY METHYL RADICALS

PAUL KEBARLE AND W. A. BRYCE

The effect of the addition of mercury dimethyl on the rates of decomposition of 1-butene- and 1-butene-4-d_3 has been investigated as part of a detailed study of the pyrolysis of these two compounds. The reactions were carried out in a static system in a quartz reactor at temperatures around 500° C. The composition of the reaction mixture was determined at various time intervals by gas chromatography. In the studies with 1-butene-4-d_3, the reaction products separated by gas chromatography were collected and analyzed in a 90° Nier-type mass spectrometer to determine the distribution of deuterium in the various isomeric products.

The principal products of the 1-butene pyrolysis were methane, propylene, ethylene, ethane, and a number of C_5 to C_7 unsaturated hydrocarbons mostly with cyclic structures. The addition of 5% by volume of mercury dimethyl to the 1-butene was found to accelerate greatly the formation of practically all reaction products. The concentrations of the C_1 to C_3 hydrocarbon products for the normal and sensitized decomposition of 1-butene at 492° C. as a function of reaction time are shown in Fig. 1. The initial pressure of the reactant was 200 mm. of mercury in each experiment. The C_1 to C_3 hydrocarbons accounted for approximately 70 to 80% by volume of the total reaction products at the above temperature. The effect of the sensitizer on the rate of formation of the C_1 to C_3 decomposition products can be seen in a comparison of the concentration of each substance at 1 minute reaction time in the sensitized and unsensitized decompositions under similar reaction conditions. These results are given in Table I.

At the temperature of the experiment mercury dimethyl undergoes rapid decomposition resulting in the formation of free methyl radicals. Thus, the acceleration of the butene decomposition in the sensitized reaction is certainly due to "forced" free radical reactions brought about by the methyl radicals. The fact that the addition of methyl radicals

results in the accelerated formation of all products already formed in the unsensitized decomposition suggests that the normal decomposition also proceeds by a radical mechanism in which methyl radicals play an important part.

The free radical decomposition of 1-butene involving the primary step [1] has been detected at high temperatures (1000 °C.) with the mass spectrometer (3):

$$CH_3—CH_2—CH=CH_2 \rightarrow CH_3 + CH_2—CH=CH_2. \qquad [1]$$

The activation energy and frequency factor of reaction [1] have been determined with the toluene carrier technique for the temperature range 650–770° C. (5). However, the

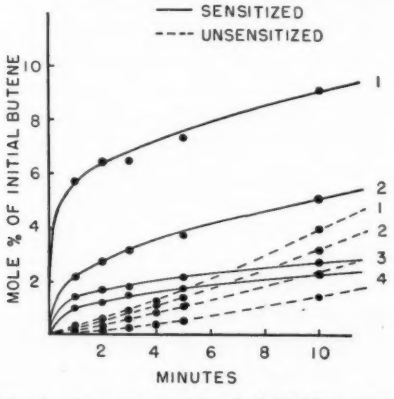

FIG. 1. The effect of sensitization by mercury dimethyl (5% by volume) on the rate of formation of light hydrocarbons in the pyrolysis of 1-butene. 1—Methane. 2—Propylene. 3—Ethylene. 4—Ethane.

lack of inhibiting effect by nitric oxide on the thermal decomposition at lower temperatures (550° C.) (4) has been considered as an indication that, at these temperatures, the decomposition proceeds by a molecular mechanism (2). As was pointed out above, the results of the mercury dimethyl sensitized reaction suggest that, at these lower temperatures also, the reaction proceeds by a free radical mechanism. This is further borne out in the results from the 1-butene-4-d_3 experiments.

TABLE I

Compound	Concentration ratio, sensitized to unsensitized reaction (after 1 minute)
CH_4	13.3
C_2H_6	11.4
C_2H_4	7.1
C_3H_6	9.7

In preliminary experiments, the thermal decomposition of the 1-butene-4-d_3 was compared with that of undeuterated 1-butene. No significant differences were found in the rates of decomposition and rates of product formation for the two compounds.

The deuterium distribution in the C_1 to C_4 reaction products from the normal and mercury dimethyl sensitized decomposition of the 1-butene-4-d_3 at 492° C. for 1 minute reaction time is shown in Table II. For the sensitized reaction, the concentrations of the

TABLE II

Compound	Concentration in mole per cent (×10) of initial 1-butene-4-d_3		Concentration ratio, sensitized to unsensitized
	Unsensitized	Sensitized	
CD_4	0.11	0.7	7
CD_3H	2.77	17.2	6
CD_2H_2	1.09	8.3	8
CDH_3	0.06	1.6	27
CH_4	0.30	29.8	100
$C_2D_4H_2$	0.05	0.3	6
$C_2D_3H_3$	0.56	7.1	13
$C_2D_2H_4$	0.22	2.1	10
C_2D_3H	0.10	0.9	9
$C_2D_2H_2$	0.29	2.3	8
C_2DH_3	0.32	2.0	6
C_2H_4	1.34	9.5	7
$C_3D_4H_2$	0.07	0.6	9
$C_3D_3H_3$	0.14	3.8	27
$C_3D_2H_4$	0.17	1.7	10
C_3DH_5	1.75	8.3	5
C_3H_6	0.16	7.5	47
C_4H_8	—	27.0	

compounds are given in mole per cent of the initial 1-butene-4-d_3. The reactant 1-butene-4-d_3 contained 9% 1-butene-4-d_2 as an impurity (1). The mass spectrometric analysis of the deuterium compounds was facilitated by the complete separation of the methanes from the ethanes, the ethanes from the ethylenes, etc., by means of gas chromatography. However, the lack of published spectra for some of the deuteroisomers, particularly the deuteroethanes, for which measurements of the molecular (parent) masses at low electron energies are also not applicable, resulted in some uncertainties in the concentration data given in Table II. These data should be considered as having a semiquantitative significance only.

The results in Table II show that deuterium mixing has occurred to a surprisingly large extent. In the non-sensitized decomposition of the 1-butene-4-d_3, only approximately 1% of the reactant had decomposed. For this case, the effect of secondary reactions involving stable reaction products should be insignificant. Therefore, the large extent of deuterium mixing is probably the result of a complex free radical mechanism.

It is interesting to note that, in the sensitized reaction, a relatively large quantity (2.7%) of undeuterated butene was formed. This product was not observed in the normal decomposition of the 1-butene-4-d_3. The mechanism proposed to explain the formation of undeuterated butene is the following:

$$Hg(CH_3)_2 \rightarrow Hg + 2CH_3, \qquad [2]$$

$$CH_3 + CH_2{=}CH{-}CH_2{-}CD_3 \rightarrow CH_3{-}CH_2{-}CH{-}CH_2{-}CD_3, \qquad [3]$$

$$CH_3{-}CH_2{-}CH{-}CH_2{-}CD_3 \rightarrow CH_3{-}CH_2{-}CH{=}CH_2 + CD_3. \qquad [4]$$

In addition to explaining the formation of undeuterated butene, the mechanism provides CD_3 radicals, which should account to a large extent for the increased rate of formation of CD_3H and CD_4 (and possibly other products containing CD_3 groups) in the sensitized reaction. A similar reaction has been suggested in the reaction of methyl radicals with propylene (6).

Addition of the methyl radical to the secondary carbon of the double bond in 1-butene-4-d_3 could result in alternative modes of decomposition of the $C_5H_8D_3$ radical:

$$CH_3 + CH_2{=}CH{-}CH_2{-}CD_3 \rightarrow CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2{-}CD_3, \qquad [5]$$

$$CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2CD_3 \rightarrow CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{CH}} + CH_2CD_3. \qquad [6]$$

Reaction [6] would result in an increased rate of formation of both propylene and CH_2CD_3, in qualitative agreement with the results given in Table II.

The possible occurrence of reactions [3] to [6] indicates that, in the temperature range studied, free radical addition to the double bond of an olefin is not necessarily inactive for the mechanism, i.e. the addition product does not exclusively decompose to yield back the original radical and olefin. The newly formed bond in the addition may be retained and the addition product may decompose with the splitting of a different bond leading to the formation of a new olefin and a new radical. Such disproportionation reactions might be of considerable importance in mechanisms for the thermal decomposition of olefins.

A full account of the results obtained in the investigation of the pyrolyses of 1-butene and 1-butene-4-d_3 will be published.

We are grateful to Dr. L. C. Leitch of the National Research Laboratories, Ottawa, for the synthesis of the 1-butene-4-d_3, to the Defence Research Board for financial support (D.R.B. Project No. D44-50-01-10), and to Mr. S. A. Ryce for assistance with the gas chromatographic analysis.

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Received March 6, 1957.
Department of Chemistry,
University of British Columbia,
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